ANL-5924
Chemistry - Separation
Processes for Plutonium
and Uranium
(TID-4500, 14th Ed.)
AEC Research and
Development Report

ARGONNE NATIONAL LABORATORY
P. O. Box 299
Lemont, Illinois

CHEMICAL ENGINEERING DIVISION
SUMMARY REPORT

July, August, September, 1958

Stephen Lawroski, Division Director

W. A. Rodger, Associate Division Director
R. C. Vogel, Associate Division Director
V. H. Munnecke, Assistant Division Director

December, 1958

Preceding Quarterly Reports:

ANL-5896	April, May, June, 1958
ANL-5858	January, February, March, 1958
ANL-5820	October, November, December, 1957

Operated by The University of Chicago
under
Contract W-31-109-eng-38

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency Thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

DISCLAIMER

Portions of this document may be illegible in electronic image products. Images are produced from the best available original document.

TABLE OF CONTENTS

	<u>Page</u>
SUMMARY	11
I. FLUORIDE VOLATILIZATION SEPARATIONS PROCESSES . . .	22
A. Laboratory Investigations	23
B. Pilot-Plant Studies	43
C. Corrosion Studies.	48
II. LIQUID METAL-FUEL REPROCESSING.	53
A. Extraction of Uranium and Fission Products from Bismuth	54
B. Bismuth Fluoride Chemistry	60
III. FLUIDIZATION STUDIES.	61
A. Separation of Uranium from Zirconium-Uranium Fuel Alloys	62
B. Calcination of Reactor Fuel-Processing Wastes.	75
C. Mixing Studies in Straight and Tapered Fluidized Beds.	85
D. Study of the Factors Influencing Particle Growth in a Fluid-Bed Calciner.	86
IV. REACTOR CHEMISTRY.	88
A. Metal Oxidation-Ignition Kinetics	89
B. Metal-Water Reactions	105
C. Reactor Decontamination	108
D. Neutron Capture Cross Section of U^{238}	115
E. Determination of Alpha in EBR-I.	116
V. CHEMICAL-METALLURGICAL PROCESSING.	118
A. Laboratory Studies	122
B. Semi-Works Studies of High-Temperature Processes	149
C. Fuel-Processing Facilities for EBR-II.	166

TABLE OF CONTENTS

	<u>Page</u>
VI. ANALYTICAL RESEARCH AND SERVICES	174
A. Analytical Service and Development.	174
B. Analytical Research	181
VII. ROUTINE OPERATIONS	183
A. Waste Processing.	183
B. Gamma-Irradiation Facility	184

LIST OF TABLES

<u>No.</u>	<u>Title</u>	<u>Page</u>
1	Fluorination of Mixtures of Plutonium Tetrafluoride and Uranium Tetrafluoride.	26
2	Pertinent Data on Samples of Uranium Dioxide Used in the Fluorination Experiments.	29
3	Fluorination of Uranium Dioxide.	31
4	Weight-Change Data on the Thermal Decomposition of Plutonium Hexafluoride.	37
5	Chemical Analyses of Plutonium Hexafluoride Thermal Decomposition Product.	38
6	Pressure Change during the Thermal Decomposition of Plutonium Hexafluoride.	39
7	Bulk Densities of Plutonium Tetrafluoride Samples from Several Sources.	40
8	Fluorination Rates of the Solid Thermal Decomposition Product of Plutonium Hexafluoride.	41
9	Comparative Fluorination Rates of Plutonium Tetrafluoride from Several Sources.	41
10	Comparison of Mass-Transfer Coefficients for Various Draft-Tube Configurations.	48
11	Comparative Corrosion of Several Nickel Alloys in Fluorinated Fused Fluorides.	50
12	Corrosion of "L" Nickel and Hastelloy B in Fluorinated Fused Fluoride: Liquid Phase and Interface Attack.	51
13	Corrosion of "L" Nickel and Hastelloy B in Fluorinated Fused Fluoride: Maximum Vapor-Phase Attack.	51
14	Analysis of Sodium Fluoride-Zirconium Fluoride Fused Salt.	55
15	Extraction of Uranium from Bismuth with Sodium Fluoride-Zirconium Fluoride.	55

LIST OF TABLES

<u>No.</u>	<u>Title</u>	<u>Page</u>
16	Reduction Effect of Magnesium on Uranium Tetrafluoride in Molten Sodium Fluoride-Zirconium Fluoride	57
17	Extraction of Cerium from Bismuth with Sodium Fluoride- Zirconium Fluoride	58
18	Extraction of Bismuth Alloys with Zinc	59
19	Volatile Material Evolved during Heating of Fluid-Bed Dried Zirconium Fluoride	66
20	Elemental Analyses of Fluid-Bed Dryer Products	67
21	Ruthenium Decontamination Factors across the Venturi Scrubber and Silica Gel Adsorber	76
22	Ruthenium Material Balances	76
23	Results of Corrosion Tests of Sintered Stainless Steel Type 316 Exposed to Simulated Off-Gases of Waste Calcination Process	83
24	Comparison of Effects of Specific Area and Aluminum and Copper Additives on Ignition Temperatures in Oxygen.	91
25	Impurity Content of Uranium	93
26	Electrical Heating of Zirconium and Zirconium-1.08 Atom Per Cent Titanium Alloy Foils	99
27	Oxidation of Zirconium-Base Alloys Which Follow the Cubic Rate Law with No Breakaway	103
28	Oxidation of Zirconium-Base Alloys Which Show Breakaway at 700 C and 200 mm Oxygen	104
29	Preliminary Runs: Metal-Water Reactions, Condenser Discharge Method.	106
30	Adsorption of Activity on Metal Samples in EBWR Steam Condenser During First Fuel-Defect Test.	113
31	Results of Several Decontamination Procedures on EBWR Samples	114

LIST OF TABLES

<u>No.</u>	<u>Title</u>	<u>Page</u>
32	U^{238} Capture Cross Sections	116
33	Analyses of Iodine Isotopes Volatilized during Melt Refining . .	123
34	Distribution of Iodine in Melt Refining	125
35	Distribution of Antimony in Melt Refining	126
36	Analytical Results for Uranium-Zirconium Carbide Melt.	127
37	Activity Coefficients of Uranium in Zinc Solutions	133
38	Coprecipitation by U_2Zn_{17} from Liquid Zinc.	136
39	Effect of Aluminum Addition on Zirconium Concentration of a Zirconium-Uranium-Zinc System	137
40	Rate of Reaction of Uranium with Liquid Zinc	140
41	Effect of Time on Distribution of Elements between Zinc - 0.2 Weight Per Cent Magnesium and Dow 230 Flux.	142
42	Summary of Calibration Experiments with Benzoic Acid	147
43	Results of Zirconium Removal Runs	150
44	Results of Pyrozinc-Magnesium Process Experiments	155
45	Non-Stagnant Corrosion Tests of Several Metals in Molten Magnesium	161
46	Spectrographic Analysis of Surface Film on Tantalum after Exposure to Molten Magnesium.	162
47	Light Emission from Gamma-Irradiated Incandescent Lamps. .	168
48	Summary of Melt-Refining Furnace Runs	170
49	The Indirect Polarographic Determination of Plutonium	176
50	The Spectrophotometric Determination of Plutonium (VI) with Ferrous Orthophenanthroline	176

LIST OF TABLES

<u>No.</u>	<u>Title</u>	<u>Page</u>
51	The Spectrophotometric Determination of Plutonium (VI) with Iodide	177
52	A Comparison of the Nitric Acid and Amalgam-Leach Dissolutions of Bismuth Alloys	178
53	Ultrasonic Decontamination of Cave Equipment	179
54	Additional Analytical Methods for EBR-II Processing Control .	180
55	Analytical Methods for EBR-II Steam-System Water Analysis .	181
56	Thermal Neutron Capture Cross Section of Cesium-137	182
57	Summary of Number of Samples and Units for July, August and September in High-Level Gamma-Irradiation Facility	184

LIST OF FIGURES

<u>No.</u>	<u>Title</u>	<u>Page</u>
1	Combined Aqueous Dissolution - Fluoride Volatility Scheme (ADF Process)	24
2	Apparatus for the Fluorination of Uranium Oxides by Elemental Fluorine.	29
3	Fluorination of Uranium Dioxide	31
4	Apparatus for Plutonium Hexafluoride Decomposition Studies. .	34
5	Apparatus for Fluorine Consumption Experiments	42
6	Consumption of Fluorine by a Nickel Vessel	43
7	Dropwise Fluorinator Process Concept	45
8	Typical Thickness Contour of "L" Nickel Subjected to Fluorinated Sodium Fluoride-Zirconium Fluoride at 600 C . . .	52
9	Summary of Runs Made in Six-Inch Fluid-Bed Dryer	64
10	Results of the Fluorination-Volatilization of Uranium from Dried Uranium-Zirconium Mixtures	69
11	Vertical Contour of Nickel Corrosion Support Tube in Fluid-Bed Fluorinator.	70
12	Photomicrographs of Fluid-Bed Dryer Products	72
13	Photomicrographs of Fluid-Bed Fluorination Products	73
14	The Change in Venturi Scrubber Recycle Scrub Solution Normality and Activity with Hours of Usage	77
15	Regeneration of Silica Gel Adsorber	78
16	Pressure Drop across Sintered Metal Filters While in Operation with Automatic Venturi Blowback Device	80
17	Representative Cross Sections of Failed Sintered Stainless Steel Filter from Fluid-Bed Calciner.	81
18	Section of Type 347 Stainless Steel Fin Used to Divide Filter Elements into Groups.	82

LIST OF FIGURES

<u>No.</u>	<u>Title</u>	<u>Page</u>
19	Schematic Diagram of Corrosion Test Unit for Sintered Stainless Steel Filters	83
20	Type 316 Sintered Stainless Steel after Exposure to Simulated Waste Calciner	84
21	Burning Curves for Argonne-Base Uranium in Oxygen	90
22	Uranium Ignition Temperatures in Helium-Oxygen Mixtures . .	92
23	Burning Curves for Argonne-Base Uranium in Oxygen and 20 Per Cent Oxygen - 80 Per Cent Nitrogen Mixture.	94
24	Ignition Temperatures of Argonne-Base Uranium in Helium-Oxygen and Nitrogen-Oxygen Mixtures	94
25	Oxidation of Uranium at 200 C in 200 mm Oxygen for Designated Times.	96-97
26	Zirconium Electrical Heating Apparatus.	98
27	Oxidation of Various Zirconium-Base Alloys at 700 C and 200 mm Oxygen: General Oxidation Characteristics.	102
28	Design of High-Pressure Autoclave for Study of Static Metal-Water Reactions in TREAT	107
29	Half Life of 0.51 Peak (Copper Samples).	111
30	Half Life of 0.51 Peak (Mild Steel Sample)	111
31	Portion of Net Gamma-Ray Spectrum of Np^{239} (after electronic subtraction of spectrum due to uranium and its daughters)	115
32	Neutron Capture Cross Section of U^{238}	117
33	Assemblies for Collection of Volatilized Iodine-Bearing Material.	123
34	Photomicrograph of Vertically Sectioned Ingot: Uranium-Zirconium Carbide Melt	128

LIST OF FIGURES

<u>No.</u>	<u>Title</u>	<u>Page</u>
35	Undercutting of Boron Nitride by Molten Uranium	129
36	Cadmium-Uranium Phase Diagram at One Atmosphere Pressure	130
37	Cell emf as a Function of Uranium Content of Uranium-Zinc Electrode	135
38	Reaction of Uranium Metal with Molten Zinc	139
39	Effect of Rotational Velocity on Rate of Reaction of Uranium with Molten Zinc	139
40	Reduction of Uranium Dioxide Pellets by Zinc - 6.12 Per Cent Magnesium Alloy at 730 C.	141
41	Pyrozinc-Magnesium Separation Process: Results of Experiment 1.	156
42	Pyrozinc-Magnesium Separation Process: Results of Experiment 2.	156
43	Pyrozinc-Magnesium Separation Process: Results of Experiment 3.	157
44	Liquid Magnesium Circulating Loop.	160
45	Cross Section Showing Surface Film Formation on Tantalum after Exposure to Molten Magnesium.	162
46	Zinc-Vaporization Apparatus	165
47	Cross-Sectional View of Insulated Melt-Refining Crucible	170
48	Remote Micro Pipetter	180

CHEMICAL ENGINEERING DIVISION SUMMARY REPORT

July, August, and September, 1958

SUMMARY

I. Fluoride Volatilization Separations Processes (pages 22 to 52)

A new reprocessing scheme which may be applicable to most power reactor fuels is described. The irradiated fuel is dissolved in an appropriate aqueous solution which is then calcined to a mixture of dry oxides. Fluorination of this mixture ultimately produces the hexafluorides of uranium and plutonium, which are volatilized. This process will be called the ADF (aqueous dissolution and fluorination) process.

Several physical and chemical techniques appear to be available for the separation, decontamination, and purification of the uranium and plutonium fluorides. The inherent versatility of the ADF scheme suggests its potential application to a variety of fuel element materials and fuel cycles.

In connection with this potential reprocessing scheme, the fluorination rates of uranium tetrafluoride-plutonium tetrafluoride mixtures were investigated. The results indicate that the conversion rate of uranium tetrafluoride to the hexafluoride by elemental fluorine is not affected by the presence of plutonium tetrafluoride. However, the rate of plutonium hexafluoride formation may be decreased due to its reduction by uranium tetrafluoride.

Since oxides, as well as fluorides, are involved in this scheme, fluorination rate studies were conducted on uranium dioxide. Short fluorinations at low temperatures with elemental fluorine appeared to produce uranium hexafluoride directly, while longer periods of exposure and higher temperatures produce uranyl fluoride as an intermediate compound in the reaction.

The thermal decomposition of plutonium hexafluoride is of importance in assessing its behavior in a process. The stoichiometry of the decomposition reaction at 300 C was investigated by several methods that showed the reaction products to be fluorine and plutonium tetrafluoride. This plutonium tetrafluoride was fluorinated to the hexafluoride by elemental fluorine at approximately the same rate as plutonium tetrafluoride from Rocky Flats.

A brief study was made on the rate of fluorine consumption by nickel vessels at temperatures from 300 to 600 C. The reaction rate proved to be time-dependent and an activation energy of five to ten kcal-mole was estimated.

Development work has continued on the fused fluoride process for the recovery of enriched uranium from zirconium-matrix fuel alloys. The alloy is dissolved by immersing it in molten sodium fluoride-zirconium fluoride at 600 C and passing hydrogen fluoride vapor through the system. The dissolved uranium tetrafluoride in the melt is then volatilized as uranium hexafluoride by sparging with fluorine. The uranium hexafluoride product is purified and decontaminated by fractional distillation.

Installation of a graphite dissolver-hydrofluorinator for pilot plant dissolution tests is continuing.

Studies of alternate methods of contacting in the fused salt fluorination step are under way, with the aim of minimizing corrosive conditions. In one scheme under consideration, dropwise fluorination is carried out by spraying molten salt into a fluorine atmosphere. Preliminary estimates of mass-transfer steps involved indicate a range of conditions in which the process may be feasible. Spraying tests show that salt droplets of 60-micron diameter can be produced. Equipment has been assembled for further tests.

Another scheme involves the use of a frozen salt wall to serve as container of the fused salt during fluorination. Several means of internal electrical heating are under consideration. Induction heating has the advantage of requiring no metal components in contact with the fused salt. Efficient power input to a six-inch diameter liquid charge has been demonstrated for 350-kc power. A stable frozen wall has been achieved on a small-scale induction heating test. Tests on a larger scale are planned.

Sparging tests with a mock-up system indicate that a draft tube is not necessary for good contact between vapor and liquid in the fluorinator. This allows a simpler design.

Further corrosion data are reported on the behavior of nickel and nickel alloys in fluorinated sodium fluoride-zirconium fluoride at 600 C. Nickel-molybdenum alloys (Hastelloy B and INOR-1) show relative immunity to intergranular attack when compared to "L" nickel and "D" nickel in liquid phase and interface exposure. Dimensional changes are about comparable in the four materials tested.

II. Liquid Metal-Fuel Reprocessing (pages 53 to 60)

Laboratory work to demonstrate the practicality of the fused fluoride volatility process for the LMFR fuel is being continued. Attention is being given to experiments which will establish the mechanism and conditions for the removal of cerium (representative of the rare earths), uranium and zirconium from bismuth by extraction with molten mixtures of zirconium fluoride and sodium fluoride.

The rapid extraction of uranium from bismuth, very low in magnesium concentration, has been quantitatively demonstrated. Equilibration experiments have been performed in which alloys of uranium in bismuth (simulating the concentration of uranium in the LMFR fuel) have been contacted with the molten sodium fluoride-zirconium fluoride salt at 600 C. The uranium concentrations have been lowered to values lower than the blank (apparent) uranium values obtained for pure bismuth equilibrated with the fused salt.

Magnesium, which will be present as an antioxidant in the LMFR fuel, was shown to be incapable of reducing uranium tetrafluoride to uranium and causing its back extraction into bismuth.

Extraction of cerium from bismuth, low in magnesium concentration, by the molten fluoride salt has also been accomplished. Good extraction factors are obtained in short contact times.

Preliminary information, based on autoradiographic tests, indicates that radioactive zirconium can be extracted from bismuth with the molten fluoride salt.

The partial extraction of uranium and radioactive ruthenium from bismuth with zinc has been demonstrated. The extraction of cerium from bismuth with zinc has been shown not to occur.

Bismuth pentafluoride has been prepared by the direct reaction of fluorine with bismuth. The stoichiometry of the compound has been approximately established by determining the approximate amount of fluorine which has reacted with a known weight of bismuth. The crude bismuth pentafluoride can be purified by sublimation.

III. Fluidization Studies (pages 61 to 87)

Development work on the process for the recovery of uranium from low uranium-high zirconium alloys (ADF process) was continued. The process includes aqueous dissolution, fluid-bed drying and fluid-bed fluorination of the uranium to the hexafluoride. Runs in the six-inch diameter fluid-bed dryer were made at 300 C using feed solutions containing the equivalent of five and ten weight per cent uranium alloys. The drying unit was also operated successfully at 240 C, thus extending the process operating temperature range to 240 to 450 C. Refractory-grade zirconium oxide and calcium fluoride were compared as starting bed materials. Generally the oxide was more satisfactory. Some particle growth occurred in the bed, but at a rate which did not interfere with operations.

As a part of a study to correlate uranium removal during fluorination with species of zirconium fluoride formed at various drying temperatures, identification of fluid-bed dryer products was attempted. X-ray diffraction studies of products prepared from feed solutions containing a fluoride-to-zirconium mole ratio of ten indicate several polymorphic forms of zirconium tetrafluoride might be formed at 300 C, while zirconyl fluoride is formed at 450 C. A series of ignition tests was made at 450 C on materials dried at 300 C. Both water and hydrofluoric acid were evolved in small and varying amounts.

Fluorinations in the 2½-inch diameter fluid-bed unit succeeded in removing about 99 per cent of the uranium in four hours at 600 C and 12 hours at 500 C from materials prepared in a fluid-bed dryer at 300 C. Equivalent results were achieved on material dried at 240 C. The feed contained the equivalent of five and ten weight per cent uranium alloys. Poor uranium removal was achieved in a run at 500 C on fluid-bed dried material containing precipitated uranium-tetrafluoride (3.5 weight per cent alloy equivalent).

Laboratory fluorination studies showed metal additives to uranium-zirconium feed solutions had no inhibiting effect on uranium volatilization. A single laboratory experiment was performed in which 20 moles of carbon per mole of uranium were added to the feed. About 87 per cent of the uranium volatilized while 96 per cent of the carbon was removed in two hours of fluorination at 600 C.

In the fluid-bed waste calcination process currently under investigation, liquid radioactive wastes are spray injected into a heated fluidized bed of solid particles. During the last quarter, emphasis has been placed on determining the efficacy of a venturi scrubber and a silica gel adsorber in removing ruthenium from the calciner off-gas. A series of runs has been made using ruthenium-106 as tracer in a synthetic feed. The scrubber and adsorber removed ruthenium from the off-gas by factors of 500 to 800.

Preliminary experiments have been completed in the radioactive tracer mixing studies carried out in straight and tapered fluidized beds using copper metal powder and granules. The rate of mixing followed the diffusion equation in the straight column but not in the tapered column. A mixing coefficient of 0.005 sq ft/sec, independent of gas velocity, was obtained in the straight column. The rate of mixing was retarded in the tapered bed, although there was an increase with increasing flow rate. The minimum fluidizing velocity was higher in the tapered bed, and slugging and bed expansion were reduced.

A study of the factors influencing particle growth in a fluid-bed calciner was started. Initial experiments were conducted with sodium carbonate solutions using a three-inch diameter column. Microscopic

examination of dried particles disclosed no growth rings such as had been observed with products from uranyl nitrate and zirconium fluoride solution calcinations.

IV. Reactor Chemistry (pages 88 to 117)

The study of factors influencing pyrophoricity and oxidation of the reactor materials: uranium, zirconium, thorium, and plutonium, has continued to progress.

In the uranium burning-curve test, variation of the oxygen flow rate has shown a negligible effect. However, decrease of the heating rate causes a decrease of the ignition temperature, indicating that burning-curve ignition test results should only be used for the comparisons of other variables.

The specific area dependence appears to dominate the additive influence, since the effect of additives of aluminum and copper on the ignition temperature of 8.5-mm uranium cubes in oxygen were not shown for 0.25-mm foils. In an effort to understand the thermocycling phenomena observed when uranium reacts with air, studies in helium-oxygen and nitrogen-oxygen mixtures have been undertaken. Startling differences have been shown between the reactions in the two systems and between the reactions of two sources of pure uranium. Continued studies include the use of very high-temperature thermocouples to measure the maximum burning temperature of the metal.

The microscopic observation of the surface during isothermal oxidation of uranium suggests two simultaneous processes are involved.

An ignition test has been developed in which zirconium foil specimens were electrically heated to a high temperature in very short times. The ignition, current, and voltage were simultaneously recorded by means of oscilloscopes and a Fastax camera. Preliminary tests have shown marked differences between the behavior of both zirconium and a titanium-zirconium alloy in both oxygen and air. Zirconium shielded-ignition tests using vacuum for prevention of oxidation during heating, or using annealing to produce an unoxidized surface (by dissolving oxide into the zirconium), have not produced lower ignition temperatures than helium shielded tests.

The oxidation of 60 binary zirconium alloys has been completed. The effects of each of the 20 additives in concentrations of 1, 2, and 4 atom per cent are compared in terms of breakaway phenomena, cubic and parabolic rate constants, and total weight gain. Only copper, nickel, beryllium, and hafnium alloys showed increased oxidation resistance when compared with pure zirconium. The largest group of alloys, including pure zirconium, followed the cubic rate for the entire extent of reaction up to 1400 minutes.

The second largest group showed breakaway phenomena after initially following the cubic rate law. Some of the alloys followed the parabolic rate law with subsequent breakaway.

A short-term study of magnesium ignition has shown disagreements with the results of earlier experimenters. Shielded ignition tests were used to obtain an indication of an activation energy which suggests a magnesium vaporization process.

The experimental program to determine rates of reaction of molten reactor fuel and cladding metals with water is continuing. The principal laboratory-scale method involves the rapid melting and dispersion of metal wires in a water or steam environment by a surge current from a bank of condensers. The proposed method was presented in detail in the previous quarterly report, ANL-5896, page 101. Preliminary experience with the completed condenser discharge is reviewed. Equipment for use in the in-pile (TREAT) tests has been designed and is under construction.

A program has been undertaken with the Reactor Engineering Division to determine the feasibility of decontamination of the auxiliaries of a boiling water reactor following a fuel rupture. Coupons have been inserted into several locations in the EBWR for identification of activities and for decontamination studies. Laboratory autoclaves are now in use, and a pilot-plant loop that simulates reactor operation is being constructed and installed in a shielded cell.

The relative values of the neutron-capture cross section of U^{238} for monoenergetic neutrons in the energy range 0.36 to 1.50 Mev have been determined. The purpose of this work was to determine whether the small peak in the curve in BNL-325 in the region around 1 Mev is a real effect. The existence of the peak was corroborated.

V. Chemical-Metallurgical Processing (pages 118 to 173)

Melt refining, liquid metal extraction and intermetallic crystallization are now being examined as direct-cycle pyrometallurgical methods of processing nuclear reactor fuels.

Melt refining consists of melting the discharged fuel and holding it molten for a period of time. Decontamination is effected by oxide drossing and volatilization of rare gases and low-boiling fission products. Detailed laboratory studies of the behavior of iodine in the melt-refining process have been made. In molten uranium, isotopic mixing of fission product iodine and inert iodine added as uranium triiodide takes place rapidly and quantitatively. Iodine at EBR-II concentration level is almost completely

(98 per cent) removed from the ingot and skull after three hours at 1400 C. Volatilization of iodides of the alkaline earth and rare earth metals is the chief mechanism.

Antimony, as tracer, has been found not to be separated from uranium under nominal melt-refining conditions.

The joint solubility of zirconium and carbon in molten uranium is under examination. Two four-run series for demonstrating zirconium removal in graphite-coated crucibles were completed in the semi-works using liquation periods of three hours and five hours at 1400 C. Zirconium removals of around 50 per cent were realized from charges initially 0.7 weight per cent in zirconium. About 10 per cent higher removals were obtained with the longer liquation time. Yields for all runs varied between 90 and 93 per cent. Cerium removal, also followed in these runs, was not adversely affected by the presence of the graphite coating, being above 90 per cent in all runs from charges of 0.7 weight per cent cerium.

Melting of oxide-coated pins continues to be more difficult than the melting of massive metal. These coatings interfere with uranium coalescence in the melting operation and lower ingot yields by entrapping metal in the pouring operation. Calcium is effective in reducing the oxide, but attacks zirconia crucibles excessively. This may make necessary a pre-melting operation in an inert crucible, such as tungsten or beryllia, to effect coalescence of the uranium and provide a satisfactory charge for the melt-refining operation.

A silicon nitride, silicon-carbide-impregnated graphite susceptor supplied by National Carbon Co. has shown excellent resistance to sodium vapor in three successive tests. Tungsten susceptors have also been obtained for testing.

A method proposed for processing uranium to separate the noble metals not removed by melt refining (ruthenium, molybdenum, etc.) is the Pyrozinc process. This process begins with the dissolution of the metal ingot in molten zinc. Uranium forms an intermetallic compound with zinc (U_2Zn_{17}) which can be separated by fractional crystallization. Zinc may be removed from the uranium-zinc intermetallic compound by vaporization. Uranium in the oxide dross from melt refining may be similarly recovered after dissolution in zinc-magnesium.

A number of supporting laboratory studies relative to the Pyrozinc process are being made. For example, cadmium has been suggested as an alternate to zinc in the Pyrozinc process. A tentative phase diagram for the uranium-cadmium system is presented. Cadmium-uranium solutions can be contained in mild steel up to at least 550 C with no evidence of corrosion.

An electrochemical cell with the most highly purified constituents available gave potential measurements at temperatures between 540 and 670 C which yield the following equation for the activity of uranium in a saturated zinc solution:

$$\log_{10} a = -15,922/T + 17.310 - 4.8465 \times 10^{-3} T$$

Two different sets of measurements have demonstrated that unsaturated solutions of uranium in molten zinc obey Henry's law to within better than 10 per cent.

Only lanthanide and actinide elements have so far been observed to coprecipitate with uranium from a zinc solution. The addition of aluminum has been shown to cause apparent precipitation of zirconium from zinc solutions.

Crystals of U_2Zn_{17} grown from solution by slow cooling through the liquidus have been shown to undergo only slight size refinement as a result of the addition of magnesium to the system.

In the application of liquid metal processing to scrap recovery, semiworks study of recovery of uranium from crucible skulls of the melt-refining process by dissolution in a six weight per cent magnesium-zinc alloy is underway. In two runs, 80 and 90 per cent of the accountable uranium was dissolved in the zinc-magnesium solution at 800 C. These recoveries are still on the low side and need to be improved. The reduction of uranium dioxide pellets by a zinc-6 weight per cent magnesium alloy was studied in the laboratory. After three hours the reduction was 87 per cent complete.

The distribution of fission products between uranium-zinc alloy and molten Dow-230 flux at 735 C is essentially complete in one hour. The results confirmed earlier findings that strontium and cesium are nearly quantitatively separated from uranium, while zirconium and ruthenium are left behind. Fifty per cent of the cerium and one per cent of the plutonium were also extracted.

The proposed process for recovery and purification of plutonium in reactor blanket material is molten magnesium extraction. The blanket uranium-alloy composition was recently changed from the low-melting (860 C) five weight per cent chromium-uranium alloy to a high-melting (around 1130 C) three weight per cent molybdenum-uranium alloy. The magnesium extraction procedure would be more difficult to carry out at the higher temperature because of accelerated attack on materials of construction and because the operating temperature is above the boiling point of magnesium which would make necessary operation under pressure. Alternative blanket processing methods are therefore being considered.

A very promising method involves the use of zinc to dissolve the blanket alloy. Separation of plutonium and uranium from solution is effected by cooling the solution to precipitate them as zinc intermetallic compounds. The precipitated material is isolated and to it is added sufficient magnesium to form the 46.5 weight per cent magnesium-zinc eutectic composition. Plutonium is soluble in this eutectic solution, while uranium is relatively insoluble.

Available results of experiments on this process, called the Pyrozinc-magnesium process, show that plutonium is well carried (95 per cent or more) on a U_2Zn_{17} precipitate in accordance with previous laboratory work. Essentially complete solution of the plutonium and simultaneous precipitation of the uranium is effected by formation of the 46.5 weight per cent magnesium-zinc eutectic.

The hydriding-dehydriding approach was again considered, since in a sense it is similar to the Pyrozinc-magnesium process. Both ultimately make plutonium available for solution in magnesium and both rely on the low solubility of uranium in magnesium for plutonium-uranium separation. However, the three weight per cent molybdenum-uranium alloy has proved to be resistant to hydriding in contrast with natural uranium which hydrided easily.

Work is continuing on application of the results of chemical-metallurgical process and development studies to design and component testing of facilities for the EBR-II fuel-processing plant.

Design of the fuel-cycle facility and review of architect-engineer drawings was continued. Shop prints are being prepared for the cell cranes. The radiation-resistant manipulator is scheduled for testing in January 1959. The manipulator removal "blister" was completed. The design of the protective shutters for the windows was completed. The purchase order for the windows has not yet been placed.

A working model of a remote luminaire for the argon cell was tested. The effect of gamma radiation on clear incandescent lamps was determined.

The operating characteristics of the melt-refining furnace were improved by using zirconia grain as a crucible-insulating material. Melt temperatures have been accurately estimated by indirect measurement using a reference thermocouple. Fifteen runs are described. An experiment was made to estimate the effect of fission product decay heating of the pins in the furnace crucible. The efficiency of the prototype fume trap was tested for both a heated and an unheated crucible lip.

A large number of shop prints were approved for the laboratory and service building. Design of auxiliary equipment continues. The design of the primary system for treating high-level liquid wastes was completed.

Laboratory studies are being made of fundamental thermodynamic properties of materials of interest in the high-temperature program. These include calorimetric studies of refractory hard metals and other compounds.

The purification and analysis of molybdenum disulfide, prior to a determination of its heat of formation by bomb calorimetry, have been successfully accomplished. The rotating bomb has been calibrated with standard benzoic acid with a precision of 0.03 per cent; some improvements in technique are being sought.

A nickel bomb for fluorine combustion studies has been assembled and tested. Combustions of metallic molybdenum and tungsten to their hexafluorides have been carried out with greater than 99 per cent completion.

VI. Analytical Research and Services (pages 174 to 182)

Coprecipitation of plutonium fluoride with lanthanum fluoride has been demonstrated to be a satisfactory method for separating "fissium" constituents from plutonium prior to its spectrophotometric determination as the nitrate.

Three indirect chemical methods for the determination of 100-microgram quantities of plutonium show promise. Reductions of plutonium (VI) with uranium (IV), iodide, and iron (II) will be followed by polarographic or spectrophotometric assays of the reaction products.

The selective solution of minor alloying constituents from bismuth alloys by leaching amalgams with hydrochloric-hydrofluoric acid mixtures has been extended to use with cerium, magnesium, zirconium, and niobium alloys.

In the development and modification of instruments for use in the EBR-II analytical cave facility, spectrophotometer modifications have been made, ultrasonic cleaning of contaminated cave equipment has been demonstrated, and a remote pipetter has been developed and tested. Additional methods have been selected, tested, and written up for use in the EBR-II analytical facility.

The thermal neutron-capture cross section of cesium-137 is being determined by irradiating cesium-137 targets and counting the cesium-138 in the presence of the target material. The determination of fission product

cesium-137 is commonly used as a measure of the number of fissions which have occurred in reactor fuels. This cross section will indicate whether a significant amount of the cesium-137 is consumed in the reactor. The present work indicates that the neutron-capture cross section of cesium-137 is low enough so that no effect on cesium-137 content will be observed in the burn-up determinations.

VII. Routine Operations (pages 183 to 184)

The operation of the radioactive waste-processing facility and the gamma-irradiation facility continued without incident.

I. FLUORIDE VOLATILIZATION SEPARATIONS PROCESSES

A new reprocessing scheme which may be applicable to most power reactor fuels is described. The irradiated fuel is dissolved in an appropriate aqueous solution which is then calcined to a mixture of dry oxides. Fluorination of this mixture ultimately produces the hexafluorides of uranium and plutonium, which are volatilized. This process will be called the ADF (aqueous dissolution and fluorination) process. Further discussion is given in Section III, page 62.

Several physical and chemical techniques appear to be available for the separation, decontamination, and purification of the uranium and plutonium fluorides. The inherent versatility of the ADF scheme suggests its potential application to a variety of fuel element materials and fuel cycles.

In connection with this potential reprocessing scheme, the fluorination rates of uranium tetrafluoride-plutonium tetrafluoride mixtures were investigated. The results indicate that the conversion rate of uranium tetrafluoride to the hexafluoride by elemental fluorine is not affected by the presence of plutonium tetrafluoride. However, the rate of plutonium hexafluoride formation may be decreased due to its reduction by uranium tetrafluoride.

Since oxides, as well as fluorides, are involved in this scheme, fluorination rate studies were conducted on uranium dioxide. Short fluorinations at low temperatures with elemental fluorine appeared to produce uranium hexafluoride directly, while longer periods of exposure and higher temperatures produced uranyl fluoride as an intermediate compound in the reaction.

The thermal decomposition of plutonium hexafluoride is of importance in assessing its behavior in a process. The stoichiometry of the decomposition reaction at 300 C was investigated by several methods which showed the reaction products to be fluorine and plutonium tetrafluoride. This plutonium tetrafluoride was fluorinated to the hexafluoride by elemental fluorine at approximately the same rate as plutonium tetrafluoride from Rocky Flats.

A brief study was made on the rate of fluorine consumption by nickel vessels at temperatures from 300 to 600 C. The reaction rate proved to be time-dependent and an activation energy of five to ten kcal/mole was estimated.

Development work has continued on the fused fluoride process for the recovery of enriched uranium from zirconium-matrix fuel alloys. The alloy is dissolved by immersing it in molten sodium fluoride-zirconium fluoride at 600 C and passing hydrogen fluoride vapor through the system.

The dissolved uranium tetrafluoride in the melt is then volatilized as uranium hexafluoride by sparging with fluorine. The uranium hexafluoride product is purified and decontaminated by fractional distillation.

Installation of a graphite dissolver-hydrofluorinator for pilot-plant dissolution tests is continuing.

Studies of alternate methods of contacting in the fused salt fluorination step are under way, with the aim of minimizing corrosive conditions. In one scheme under consideration, dropwise fluorination is carried out by spraying molten salt into a fluorine atmosphere. Preliminary estimates of mass-transfer steps involved indicate a range of conditions in which the process may be feasible. Spraying tests show that salt droplets of 60-micron diameter can be produced. Equipment has been assembled for further tests.

Another scheme involves the use of a frozen salt wall to serve as container of the fused salt during fluorination. Several means of internal electrical heating are under consideration. Induction heating has the advantage of requiring no metal components in contact with the fused salt. Efficient power input to a six-inch diameter liquid charge has been demonstrated for 350-kc power. A stable frozen wall has been achieved on a small-scale induction heating test. Tests on a larger scale are planned.

Sparging tests with a mock-up system indicate that a draft tube is not necessary for good vapor-liquid contacting in the fluorinator. This allows a simpler design.

Further corrosion data are reported on the behavior of nickel and nickel alloys in fluorinated sodium fluoride-zirconium fluoride at 600 C. Nickel-molybdenum alloys (Hastelloy B and INOR-1) show relative immunity to intergranular attack when compared to "L" nickel and "D" nickel in liquid phase and interface exposure. Dimensional changes are about comparable in the four materials tested.

A. Laboratory Investigations (R. K. Steunenber)

1. Plutonium Fluoride Studies

a. Introduction (M. J. Steindler, R. K. Steunenber)

Current developments in reactor design have resulted in a variety of suggested fuel cycles, fuel element materials and reprocessing requirements.¹ Consequently, it is appropriate to consider the possibility

¹ "Research on Power from Fusion and Other Major Activities in the Atomic Energy Programs," U.S. Atomic Energy Commission (July, 1958)

of developing a versatile separations process capable of recovering fissionable material from these various fuels. The scheme briefly outlined below is believed to show promise for this application.

This separations procedure derives its versatility from the combination of aqueous dissolution with a series of solid-gas reactions. A simplified diagram of the scheme is shown in Figure 1. Since it is not feasible to describe in detail all the possible alternatives for each step in a brief discussion, only the major ones are mentioned.

The irradiated fuel is dissolved in an aqueous solution selected on the basis of the particular composition of the fuel element. The versatility of the scheme lies in the fact that differences in the aqueous solutions used for the dissolution do not require major changes in the subsequent process steps. Most of the production-scale experience in the dissolution of reactor fuels centers around the use of nitric acid solutions for metallic uranium. Information is also available, however, on the aqueous dissolution of other fuels, such as those containing zirconium or stainless steel.^{2,3} Due to the limitations of dissolver materials, several dissolvers instead of a single universal vessel probably would be required to handle the different aqueous solutions required by the various types of fuels.

The solution from any of the dissolvers is then subjected to a calcination process in which the uranium, plutonium, fission products, and other elements in solution are converted to a mixture of dry oxides.

²Slansky, C. M., "Symposium on the Reprocessing of Irradiated Fuels Held at Brussels, Belgium, May 20 to 25, 1957," TID-7534, Book I, p. 244.

³Blanco, R. E., *ibid.*, p. 251.

A similar procedure has been conducted successfully by the Fluidization Group to calcine radioactive waste solutions in fluidized-bed reactors.⁴ Uranium trioxide and plutonium dioxide are expected to be formed in this operation. The oxide mixture is then fluorinated. This may be done by the conventional feed materials sequence of hydrogen reduction followed by fluorination with hydrogen fluoride, then with elemental fluorine.⁵ An alternative possibility is to fluorinate the calcined product directly, if this procedure proves feasible chemically and economically. Solid-gas reactions of this type have also been conducted successfully in fluidized-bed reactors.⁵ In either of these alternative routes, the uranium and plutonium are both volatilized as the hexafluorides and thereby separated from the bulk of the fission products and other materials.

The subsequent steps of the scheme involve the separation and further decontamination of uranium and plutonium. The extent of decontamination and purification demanded of these steps will be dictated by the product requirements. Decontamination may be achieved by alternate reduction and refluorination in the case of plutonium, and by distillation in the case of uranium. Various selective chemical and physical processes appear to be available by which uranium and plutonium fluorides can be separated from each other.

The final products of the separation would normally be plutonium tetrafluoride and uranium hexafluoride. The conversion of these materials to the corresponding metals or oxides is a part of the existing production technology. Although the emphasis in this discussion has been on uranium-plutonium fuels of the power-reactor type, the same scheme should be adaptable to fuels containing dilute alloys of highly enriched uranium. (see Section III, "Fluidization Studies").

b. Fluorination of Plutonium Tetrafluoride - Uranium Tetrafluoride Mixtures
(M. J. Steindler, D. V. Steidl)

In the separations scheme described above, the behavior of plutonium tetrafluoride-uranium tetrafluoride mixtures during fluorination is of interest. Previous work on the fluorination of the individual tetrafluorides is described in ANL-5896, pages 27 to 32, and in ANL-5875.

The equipment used in this study has been described previously (ANL-5875). Briefly, a 3/4-inch OD nickel tube, surrounded by a furnace was connected to a series of two nickel U-tubes, a bubbler filled

⁴Loeding, J. W., et al, "Fluidized Bed Conversion of Fuel Processing Wastes to Solids for Disposal," Proceedings of 1958 International Conference on Peaceful Uses of Atomic Energy, Geneva (paper 1922).

⁵Lawroski, S., et al, "Production of Refined UF₆ from Ore Concentrates by Fluidization and Fractional Distillation Techniques," Proceedings of 1958 International Conference on Peaceful Uses of Atomic Energy, Geneva (paper 1552).

with Fluorolube oil and a set of two traps filled with limestone. The limestone traps permitted the discharge of the gases into the building ventilation system after reaction of the excess fluorine with the limestone. Small nickel reaction boats were filled with a weighed sample of the mixed fluorides and were introduced into the furnace tube. Fluorine was then passed over the sample at the desired temperature for a measured period of time. During the course of the fluorination the U-tubes were cooled to approximately -120 C by boiling liquid nitrogen. At the end of the fluorination the sample was cooled in a helium atmosphere and the residue in the boat was weighed. The solid residue was analyzed for uranium and plutonium by wet chemical methods. The results of the initial experiments are shown in Table 1.

Table 1

FLUORINATION OF MIXTURES OF PLUTONIUM TETRAFLUORIDE
AND URANIUM TETRAFLUORIDE

Fluorine Pressure: One atmosphere
Fluorine Flow Rates: 50 to 100 cc/min
Plutonium Tetrafluoride: Rocky Flats
Uranium Tetrafluoride: Mallinckrodt

Exp.	Temp. (C)	Time (min)	Initial Weight ^d (mg)	Final Weight ^d (mg)	Nominal Comp ^a		Residue ^b		Overhead ^c		$\frac{w/o \text{ Pu (final)}}{w/o \text{ Pu (initial)}}$
					w/o Pu	w/o U	w/o Pu	w/o U	w/o Pu	w/o U	
81	100	30	69.1	69.1	0.59	75.2	0.53	76.1	e	e	0.90
82	100	60	136.2	136.7	0.59	75.2	0.61	75.2	e	e	1.03
83	100	30	111.3	111.5	3.06	71.6	3.55	73.2	e	e	1.16
84	100	60	118.5	119.0	3.06	71.6	3.89	73.9	e	e	1.27
85	200	10	149.9	145.6	0.59	75.2	0.68	76.5	8.2	91.8	1.15
86	200	30	137.8	103.6	0.59	75.2	0.79	75.4	0.7	99.3	1.34
87	200	10	111.6	107.5	3.06	71.6	3.44	72.5	22.5 ^f	77.5 ^f	1.12
88	200	30	167.0	127.9	3.06	71.6	4.86	71.8	1.1	98.9	1.59
89	300	2	162.0	93.3	0.59	75.2	1.30	74.4	0.3	99.7	2.20
90	300	4	324.7	88.4	0.59	75.2	2.53	72.6	0.1	99.9	4.29
91	300	2	240.5	119.5	3.06	71.6	6.59	68.8	1.6	98.4	2.15
92	300	4	410.2	110.6	3.06	71.6	12.5	62.1	1.0	99.0	4.08
99g	375	2	355.9	1.4	0.59	75.2	73	4.3	0.6	99.4	123
100	375	1	684.9	241.5	0.59	75.2	2.01	71.7	0.1	99.9	3.41
101	375	1	654.4	201.8	3.06	71.6	10.6	64.0	e	e	3.46

Notes

^aNominal composition calculated from mixture weights of uranium tetrafluoride and plutonium tetrafluoride, but expressed in terms of elemental plutonium and uranium. Nominal compositions were approximately one weight per cent and five weight per cent PuF_4 in UF_4 .

^bResidue composition obtained by analysis for plutonium (counting) and uranium (titration) and expressed in terms of elemental uranium and plutonium.

^cOverhead composition calculated from the loss of uranium and plutonium. The loss for each was obtained from the nominal analysis and final residue analysis and is expressed in terms of weight per cent of each element. The sum of lost plutonium (as Pu) and of lost uranium (as U) equal to 100 per cent.

^dThe initial and final weights are for the mixture of the tetrafluorides.

^eThe analytical data are not sufficiently precise to permit calculation of meaningful values. In most cases the small difference between two large numbers (initial and final U or Pu content) was positive rather than negative.

^fExperimental results are not in agreement with the rest of the data.

^gThe initial sample size was too small and hence the residual weight also small. The experiment represents fluorination carried almost to completion and hence may not be comparable with the other experiments.

A number of comments are necessary for the correct interpretation of the results.

1. Some difficulty was encountered in the preparation of a homogeneous mixture of the tetrafluorides. The samples of uranium and plutonium tetrafluorides were weighed into a plastic container and agitated until homogeneous to the eye. Subsequently, chemical analysis showed that the homogeneity was not adequate to permit calculation of precise results, particularly in those cases in which the loss of plutonium by fluorination was small. Hence, data on the composition of both the residue and the overhead for the experiments carried out at 100 C are probably not as reliable as those carried out at higher temperatures. (It should be noted that other sites have indicated similar experiences in connection with the study of mixed oxide systems.)
2. Comparison of the rate of reaction between a sample of pure uranium tetrafluoride and a sample containing some plutonium tetrafluoride is probably more valid in the case of the mixture containing the smaller amount of plutonium. Except for data obtained at 100 C, good agreement was found between the rates from this series of experiments and those calculated from the equation

$$\log_{10} \text{Rate [mg U/(sq cm)(hr)]} = 9.008 - 3406/T(K) \quad ,$$

which was derived from data on pure uranium tetrafluoride (see ANL-5896, page 28). Thus the rate of fluorination of uranium was not markedly altered by the presence of small amounts of plutonium.

3. Similar comparisons made for the rate of fluorination of plutonium tetrafluoride from mixtures and the pure compound are probably not legitimate. In order to obtain values for the rate of fluorination of plutonium tetrafluoride from the mixture, it is necessary to approximate the surface area occupied by the plutonium tetrafluoride. In the case of experiments in which the extent of fluorination is small, the area may be approximated by assuming that the per cent of the total area covered by plutonium tetrafluoride is numerically equal to the initial concentration of plutonium tetrafluoride in the mixture. As the fluorination and hence the selective removal of uranium continues, this assumption becomes less valid. Since the results obtained in the reported experiments indicate that the overhead material is composed principally of uranium, it is difficult to calculate rates for the fluorination of plutonium in terms comparable to those used in the fluorination of the pure tetrafluoride.

4. In addition to the difficulties introduced by the changing contribution of the plutonium to the total exposed surface area, the calculation of the rate of fluorination of plutonium from these mixtures is complicated by the (probable) reaction of plutonium hexafluoride and uranium tetrafluoride. At 500 K, the free energy of the reaction

is about -34 kcal/mole, according to the data given by Glassner (ANL-5750). Even recognizing the inaccuracies in the values of the free energy, it seems reasonable to assume that plutonium hexafluoride will fluorinate uranium tetrafluoride at the temperatures of the experiments recorded in Table 1. Because of the above reaction and the effect described in paragraph 3 above, the net loss of plutonium from mixtures of the tetrafluorides may not be related directly to the rates of fluorination observed on the pure constituents.

5. In addition to the points discussed under items 3 and 4 above, the magnitudes of the rates of fluorination recorded for mixtures of plutonium and uranium tetrafluorides may be different than those observed for material prepared under process conditions. It seems possible that the constituents of the solid bed produced by calcination and subsequent hydrofluorination may represent solid solutions of uranium and plutonium tetrafluorides.
6. The analytical method used for the estimation of plutonium involved alpha counting of aqueous solutions of the reaction residues. Owing to the absence of a volatile americium fluoride, the relative contribution of americium to the total alpha count of the sample increases with removal of plutoniums and uranium. In those experiments in which extensive fluorination takes place, a certain amount of error is thus introduced.

In the light of the several points mentioned above, further experimental work on this system will concentrate on the determination of the gross changes which take place in the residual solid as well as the composition of the vapor during exposure to fluorine.

c. The Fluorination of Uranium Dioxide
(M. J. Steindler, D. V. Steidl)

The possibility of fluorinating uranium and plutonium oxides directly with elemental fluorine was mentioned in Part a of this section. Experimental data on the fluorination of uranium dioxide are presented below.

The equipment used in this study is shown in Figure 2. Except for the Fluorothene traps this equipment was similar to that described previously (ANL-5875). Samples of uranium dioxide prepared by the reduction of the trioxide were obtained from the Fluidization Group of the Chemical Engineering Division. Table 2 lists the pertinent properties of the samples.

FIGURE 2
APPARATUS FOR THE FLUORINATION OF
URANIUM OXIDES BY ELEMENTAL FLUORINE

Table 2

PERTINENT DATA ON SAMPLES OF URANIUM DIOXIDE USED
IN THE FLUORINATION EXPERIMENTS

	Sample Number	
	R-3	R-25
Temperature of Preparation of UO_3 (C)	390 ^a 440 ^a	525
Conditions of UO_2 Preparation:		
Reducing Gas Mixture	$H_2:N_2 = 3$	$H_2:N_2 = 1$
Reduction Temp (C)	715	575
Reduction Time (hr)	4	^e
Ratio $H_2:UO_3$	2:1	5:3
Product Analysis	95 to 97% UO_2 ^b 3 to 5% U_3O_8	Air Reactive, U_3O_8 present ^c
Bulk Density (g/cc) ^d	4.1	3.0

^aA mixture of two batches was used to prepare R-3.

^bAnalysis as obtained from the Pilot Plant Group.

^cAnalysis by X-ray diffraction.

^dAnalysis by present workers. These values used in calculations.

^eNot available.

In a typical experiment a sample of the solid was weighed carefully into a prefluorinated nickel reaction boat, and the boat was introduced into the furnace tube. Helium, dried by passage through a cooled bed of "Molecular Sieves," was allowed to flow over the sample while the boat was being heated to the desired temperature. A mixture of solid carbon dioxide and trichloroethylene cooled both of the traps which served as receivers for uranium hexafluoride. The lines leading from the tube furnace to the traps were maintained at 100 to 200 C. By manipulation of the valve system, fluorine was substituted for helium and the fluorine flow was adjusted to the desired value. At the end of a measured time interval, the sample was allowed to cool in a helium atmosphere. The contents of the two traps were hydrolyzed with dilute aqueous nitric acid containing aluminum and were submitted for analysis. The boat was removed from the furnace tube and reweighed. When desired, samples of the solid residue were examined by X-ray powder-diffraction techniques.

The measured variables were temperature, time, initial and final sample weight, fluorine flow rate and amount of uranium present in the traps. The volume of the solid was calculated from the arithmetic average of the initial and final sample weights, together with the experimental value of the bulk density. A surface area was calculated from the above-mentioned volume and a relationship between the volume and top area was derived for the particular dimensions of the hemicylindrical boat. This area, therefore, represents the average top exposed surface of the solid throughout the reaction. The rate of uranium loss or uranium hexafluoride formation was obtained from the amount of uranium found in the trap, the calculated surface area, and the time of fluorination.

The results obtained from the fluorination of uranium dioxide are shown in Table 3 and Figure 3. The data are believed to be self-explanatory. The following conclusions and comments are made on the basis of the results:

1. For relatively short fluorination times, the low-temperature reaction of uranium dioxide produces primarily uranium hexafluoride, with little or no conversion of the dioxide to uranyl fluoride.
2. At elevated temperatures, a second reaction becomes important, namely the conversion of uranium dioxide to uranyl fluoride.
3. The rate of uranium volatilization at 375 C is in good agreement with that obtained from experiments on the fluorination of uranyl fluoride.

Table 3

FLUORINATION OF URANIUM DIOXIDE

Fluorine Pressure The atmosphere 100% fluorine
 Fluorine Flow Rates 65 to 170 cc/min constant
 throughout each experiment
 Source of Dioxide As indicated

Exp	Source ^a	Initial Weight ^b (mg)	Final Weight ^c (mg)	Temp (°C)	Time ^d (min)	Area ^e (sq cm)	X-Ray Data ^f	Volatilized ^g (mg)	Rate ^h [$\frac{\text{mg}}{\text{sq cm}} \text{ (hr)}$]
31	R-25	657.7	658.6	30	30	1.24	-	-	-
34	R-25	891.9	893.8	100	10	1.40	-	0.48	2.4
35	R-25	899.3	897.4	100	20	1.40	UO ₂ UO ₃ ⁱ	2.2	3.1
50	R-3	85.0	758.7	130	30	1.24	-	1.3	1.6
32	R-25	658.3	355.2	200	10	1.16	UO ₂ UO ₃	2.7	1460
33	R-25	1687.8	79.4	200	30	1.52	-	900	1150
38	R-3	483.3	186.4	200	10	0.91	-	270	1780
36	R-25	1083.6	837.6	300	2	1.43	-	231	4800
37	R-25	868.7	253.0	300	5	1.18	-	450	4780
39	R-3	1069.3	191.2	330	-	1.10	UO ₂ UO ₃	795	8180
44	R-25	1663.9	1.2	375	2	.69	only UO ₂	182	270
45	R-25	1249.0	66.5	375	-	1.43	UO ₂ UO ₃ ⁱ	51	4280
48	R-25	142.0	1315.7	375	-	1.1	-	147	2740
49	R-25	1014.7	498.1	375	-	1.33	-	170	4240

^aFor description see text^bInitial sample weight^cFinal sample weight^dTime of exposure to fluorine^eTop exposed surface area of sample^fObtained by L. S. Fiksdam of the Chemical Engineering Division^gUranium hexafluoride hydrolyzed and analyzed for uranium^hRate of volatilization of uraniumⁱSample R-25 UO₂ contained a minor phase of UO₃ and, except where noted UO₃ content appeared invariant^jDecrease in UO₃ content observed

FIGURE 3
 FLUORINATION OF URANIUM DIOXIDE

The rate is expressed as milligrams of uranium present in the uranium hexafluoride per hour for a square centimeter of exposed area on top of the sample

4. There probably exist two paths by which uranium hexafluoride is formed in this system. These are shown by equations (1) and (2):

At elevated temperatures, reaction (2) predominates and the rate of uranium hexafluoride formation is given by r_4 . The formation of uranyl fluoride (r_3) is quite rapid, as evidenced by the absence of uranium dioxide lines in the X-ray photographs. No evidence for the presence of significant quantities of uranium tetrafluoride or any uranium compound other than uranyl fluoride was obtained by X-ray examination of residues reacted at elevated temperatures.

It is not possible to determine the rate-controlling step at low temperatures, except to comment that the absence of uranium compounds other than the dioxide in the X-ray photographs points to r_1 . The limiting slope of Figure 3 implies an activation energy of about 25 to 30 kcal/mole for the reaction, a value greater than the 16 kcal/mole observed for pure uranium tetrafluoride. On this basis also the rate-controlling step for the reaction at low temperature is indicated to be r_1 , and r_2 may proceed relatively rapidly, leading to a low steady-state concentration of the intermediate. It may also be that the intermediate is not UF_4 , but U_2OF_8 , UOF_2 , or an as yet unidentified compound.

5. Except for results obtained at 100 C, the rates of uranium volatilization from R-3 dioxide are higher than those observed for sample R-25. It is not possible to determine which of the several factors in the histories of the samples is responsible for the differences in rate.
6. At 375 C, the rate of uranium volatilization appears to be time dependent. Both experiments carried out for five minutes gave rates greater than those carried out for two minutes. If the mechanism proposed under part 4 above is indeed applicable, this time dependence is not surprising. A fraction of the total time of an experiment is involved in the formation of uranyl fluoride, a process which by itself does not contribute to the observed rate. This time interval is relatively more important for short duration experiments than for those carried out for longer times.

It should be emphasized that these data may not extrapolate directly to other types of equipment at higher temperatures.

d. Thermal Decomposition of Plutonium Hexafluoride
(L. E. Trevorrow, W. A. Shinn)

The possibilities of a fuel-recovery process involving the volatilization of plutonium hexafluoride have been mentioned in the preceding discussions. In order to assess the chemical feasibility of such a scheme, additional information is needed on the thermal stability of plutonium hexafluoride. In addition to thermal decomposition, plutonium hexafluoride is also destroyed by the effects of the alpha particles emitted from the plutonium nucleus. The rate of radiation decomposition has been reported to be of the order of one per cent per day for solid plutonium hexafluoride and to be smaller for vapor-phase samples.^{6,7,8} At temperatures of 200 to 300 C, however, the rate of radiation decomposition is small compared to the rate of thermal decomposition.

Adams⁹ has studied certain aspects of the rate of thermal decomposition of small quantities of plutonium hexafluoride (up to 20 mg) in this Laboratory. The purpose of the present program is to extend considerably the scope of this study, using larger quantities of material.

The thermal decomposition of plutonium hexafluoride produces fluorine gas and a non-volatile solid product. Before measurements of the decomposition rate were to be attempted, it was considered advisable to identify this solid product and thus the stoichiometry of the thermal decomposition reaction. A review of various reports on the identity of the solid decomposition product indicated that the material is probably plutonium tetrafluoride. There has been some speculation, however, that intermediate fluorides similar to those in the uranium-fluorine system may be formed. The analogous plutonium fluorides would be Pu_4F_{17} , Pu_2F_9 , and PuF_5 . Some experimental evidence has been reported for the existence of Pu_4F_{17} .^{6,10}

⁶Mandleberg, C. J., et al., J. Inorg. and Nuclear Chem., 2 358-367 (1956).

⁷Florin, A. E., et al., ibid, 2, 368-379 (1956).

⁸Weinstock, B. and Malm, J. G., ibid, 2, 380-394 (1956)

⁹Adams, M. D., Steunenberg, R. K., and Vogel, R. C., "The Transfer of Plutonium Hexafluoride in the Vapor Phase," ANL-5796 (October, 1957).

¹⁰"Report of the Chemistry and Chemical Engineering Section for February, March, April, 1956," KAPL-1536, p. 63.

The existence of PuF_5 has been postulated on the basis of thermodynamic calculations;¹¹ some experimental evidence for it has been observed,¹² but the compound has not been isolated.

In the present work an attempt has been made to identify the solid decomposition product by various measurements. These include weight change, chemical analysis, pressure effects at constant volume, and X-ray identification.

Experimental

The plutonium tetrafluoride was obtained from Rocky Flats. The fluorine was obtained from commercial sources, and was passed through a bed of solid sodium fluoride in order to remove hydrogen fluoride impurity. Helium, which was used in vacuum line operations, was dried by passage through a bed of Linde "Molecular Sieves" cooled by liquid nitrogen.

The apparatus is shown schematically in Figure 4.

FIGURE 4
APPARATUS FOR PLUTONIUM HEXAFLUORIDE DECOMPOSITION STUDIES

¹¹Brewer, L., et al., "The Higher Fluorides of Plutonium," UCRL-633 (March 20, 1950).

¹²"Report of the Chemistry and Chemical Engineering Section for November, December, 1955, January, 1956," KAPL-1491, p. 53.

The apparatus was constructed of metal and was designed to operate either as a vacuum line or as a flow system. Those portions of the apparatus in which plutonium fluorides were handled were constructed from Monel diaphragm valves and nickel and Monel parts welded together. The section in which plutonium hexafluoride was prepared, purified, and handled was connected by a Teflon-gasketed flare connector to a vacuum service line. The latter consisted of one-half-inch copper tubing and an arrangement of brass high-vacuum valves which permitted the use of a mechanical vacuum pump, a VMF-20 oil diffusion pump, dry traps and vacuum gages as needed.

The plutonium hexafluoride decomposition reactions were conducted in small nickel vessels welded together from short lengths of $1\frac{1}{4}$ -inch diameter nickel tubing and $1/32$ -inch nickel sheet. Each vessel was fitted with a Hoke No. 1103 bellows valve and a $3/8$ -inch flare connector which could be attached to the vacuum line. Teflon gaskets were used below 100 C and copper ones at higher temperatures. Each vessel had a volume of about 50 ml and weighed about 150 g, which allowed it to be weighed on an analytical balance.

Pressures were measured with a mercury manometer in conjunction with a Booth-Cromer pressure transmitter and self-balancing relay.¹³ Temperatures were determined with a chromel-alumel thermocouple and a recording potentiometer.

Due to the alpha hazard involved in handling plutonium, the work was done in a glove-box assembly. Bagging techniques were used for transfers of materials into and out of the boxes. The assembly consisted of two modified Type K Blickman hoods welded together and equipped with neoprene gloves. The vacuum system for the plutonium hexafluoride preparation and decomposition studies was in one box; the analytical balance occupied the other. Prior to introducing the plutonium compounds into the apparatus, it was pretreated with fluorine at pressures of 700 to 1200 mm and temperatures of 300 to 350 C for about 15 hours.

Preparation and Purification

Plutonium hexafluoride was prepared by passing fluorine gas over plutonium tetrafluoride in the reaction tube at 550 C (see Figure 4). The product was condensed from the off-gases in traps A and B, which were cooled by a dry ice-trichloroethylene mixture. The excess fluorine passed through the Fluorolube bubbler and into a pair of disposal traps which were filled with crushed marble.

¹³Cromer, S., "The Electronic Pressure Transmitter and Self-Balancing Relay," SAM Laboratories, Columbia University, MDDC-803 (1947).

The more volatile impurities, such as hydrogen fluoride, fluorine, and carbon tetrafluoride, were removed from the product by freezing it in trap A, which was cooled by liquid nitrogen. The plutonium hexafluoride was then warmed slowly to room temperature and distilled to the adjoining trap, B, cooled by dry ice and trichlorethylene. Both the cold traps were in line with the diffusion pump (protected by cold trap E) which was operated throughout the distillation. This procedure was essentially the one used by Weinstock, et al.⁸ The purification procedure was repeated until no further lowering of the vapor pressure of the product at the ice point could be achieved. The vapor pressure of the plutonium hexafluoride product at the ice point compared with the literature values is as follows:

Florin ¹⁴	17.3 mm
Mandleberg ¹⁵	16.9, 18.8 mm (purity said to be in doubt)
Codding ¹⁶	16 mm
Malm ¹⁷	17.6 mm
This Work	17, 16, 16, 15, 15 mm.

The ice-point pressures are reported only to the nearest millimeter, as the accuracy of the pressure transmitter was limited at pressures below 20 or 30 mm. The agreement with the literature data was taken as an indication of adequate purity, since the most likely impurities all have significantly high vapor pressures at this temperature.

Procedure

1. Prefluorination: The decomposition vessel was treated with fluorine at 300 C until the rate of fluorine consumption became small. The weight change of the vessel during an additional exposure to 300 mm of fluorine at 300 C for one hour was observed to assure a negligible amount of fluorine consumption under conditions approximating those during the decomposition.
2. Weight Change: A sample of plutonium hexafluoride was vacuum distilled into a vessel located at position C. The vessel was then heated to temperature for a given period of time. It was cooled quickly in liquid nitrogen and evacuated to remove the fluorine evolved by the decomposition reaction. After reweighing, the

¹⁴Florin, A. E., "Plutonium Hexafluoride; Second Report on the Preparation and Properties," LA-1168 (November, 1950).

¹⁵Mandleberg, C. J., et al., "Plutonium Hexafluoride, Part 1: Preparation and Some Properties," AERE-C/R-1172 (April, 1953).

¹⁶Codding, J., Hawkins, N. J., and Sabol, W. W., "Purification of Plutonium Hexafluoride," KAPL-M-PF6-1 (July, 1955).

¹⁷Malm, J. G., Weinstock, B., and Weaver, E. E., "The Preparation and Properties of NpF_6 ; A Comparison with PuF_6 ," presented at American Chemical Society Spring Meeting, San Francisco, April, 1958.

vessel was evacuated at room temperature to remove the undecomposed plutonium hexafluoride. A third weighing then permitted the weights of undecomposed plutonium hexafluoride, fluorine and solid residue to be calculated by difference. Further evacuation of the vessel containing the solid decomposition product at 100 to 150 C produced no additional weight change.

3. Chemical Analysis: The vessel containing the solid decomposition product was opened with a tubing cutter. The product was weighed. The fluorine content was then obtained by a pyrohydrolysis reaction followed by titration with standard sodium hydroxide.* The remaining solid was fired and weighed as plutonium dioxide.
4. Pressure Change at Constant Volume: Initial experiments had shown that gram quantities of plutonium hexafluoride are almost completely decomposed by heating to 300 C for one hour. Thus, an independent observation on the stoichiometry of the reaction could be made by determining the pressure change accompanying the decomposition in a constant volume system.

Results and Discussion

1. Weight-Change Data: The results of the weight-change measurements obtained from the decomposition reaction at 300 C are listed in Table 4. The atomic ratio of fluorine to plutonium in the solid decomposition product was calculated, using simple stoichiometric relationships. The vessel used in Experiment 1 contained about 0.1 g of solid from a previous decomposition at 200 C. The vessel used in Experiment 2 was a new one that had received only a prefluorination treatment with fluorine. In Experiment 3, the vessel contained about 0.4 g of residue from a previous decomposition at 300 C. In all three experiments the ratio of fluorine to plutonium was found to be close to 4.0.

Table 4

WEIGHT-CHANGE DATA ON THE THERMAL DECOMPOSITION OF PLUTONIUM HEXAFLUORIDE

Decomposition Temperature: 300 C					
Decomposition Time: 1 to 2 hours					
Container Material: Nickel					
No.	Initial Wt PuF ₆ (g)	Wt PuF ₆ Decomposed (g)	Wt Decomposition Product (g)	Wt F ₂ Evolved (g)	Atomic Ratio F/Pu, from Wt Change
1	0.3522	0.3510	0.3147	0.0363	4.08
2	0.4197	0.4178	0.3717	0.0461	3.95
3	0.8720	0.8681	0.7726	0.0955	3.96

*Analyses performed by C.A. Seils, Jr., and R.M. Clarke of the Analytical Group.

2. Chemical Analysis: The ratio of fluorine to plutonium and the percentages of the constituents in the compound were obtained from the chemical analyses. The weight change during the pyrohydrolysis of the decomposition product was determined in the analysis. The data listed in Table 5 compare the fluorine to plutonium ratios found with the theoretical values for PuF_4 and Pu_4F_{17} .

Table 5

CHEMICAL ANALYSES OF PLUTONIUM HEXAFLUORIDE
THERMAL DECOMPOSITION PRODUCT

Decomposition Temperature: 300 C
Container Material: Nickel

No.	Wt of Sample Pyro- hydrolyzed (g)	Wt PuO_2 Produced in Pyro- hydrolysis (g)	Fluorine Content Analysis (g)		Gram Atoms F ^b Moles PuO_2
			Wt PuO_2 ^a Wt Sample		
1	0.2763	0.2368	0.857	0.06726	4.05
2	0.1529	0.1318	0.862	0.03758	4.06

^aTheoretical ratio wt PuO_2 /wt sample for pyrohydrolysis of $\text{PuF}_4 = 0.860$.

^bTheoretical values are: PuF_4 : 4.00 Pu_2F_9 : 4.50
 Pu_4F_{17} : 4.25 PuF_5 : 5.00

About one-fourth of Sample 1 was residue from a previous decomposition at 200 C. The remainder was from a decomposition at 300 C. Sample 2 was the result of a decomposition at 300 C.

The fluorine and plutonium percentages total 99.9 per cent for sample 1 and 100.6 per cent for Sample 2, indicating that very little moisture was taken up by the material during the weighing and transfer operations. No particular precautions were taken to exclude atmospheric moisture from the glove boxes.

3. Pressure Change: The ratio of final to initial number of moles of gas in the system was calculated, using the ideal gas law. The results of two decomposition experiments at 300 C are shown in Table 6.

Table 6

PRESSURE CHANGE DURING THE THERMAL DECOMPOSITION
OF PLUTONIUM HEXAFLUORIDE

Decomposition Temperature: 300 C
Container Material: Nickel

No.	Pressure (mm)		Temperature (k)		Pressure Ratio ^a
	Initial	Final	Initial	Final	
1	105.0	108.0	299.0	299.7	1.03
2	95.0	96.8	302.2	304.7	1.01

Pressure Ratios for Hypothetical Decomposition Reactions

Reaction					Pressure Ratio
PuF ₆	→	PuF ₄	+	F ₂	1
4 PuF ₆	→	Pu ₄ F ₁₇	+	7/2 F ₂	0.875
2 PuF ₆	→	Pu ₂ F ₉	+	3/2 F ₂	0.75
PuF ₆	→	PuF ₅	+	1/2 F ₂	0.5

^aCalculated as $\frac{P_f T_f}{P_i T_i}$ where P_i and T_i are initial pressure and temperature and P_f and T_f are final pressure and temperature.

4. X-Ray Analysis: An X-ray powder pattern of the solid decomposition product was obtained.* Sample 1 was used. The material was identified as anhydrous plutonium tetrafluoride, with no other crystalline components evident.

Conclusion

It is concluded on the basis of the various types of evidence obtained in these experiments that the solid, non-volatile product of the thermal decomposition of plutonium hexafluoride at temperatures up to 300 C is plutonium tetrafluoride.

- e. Fluorination Rate of Plutonium Tetrafluoride Produced by the Thermal Decomposition of Plutonium Hexafluoride
(M. J. Steindler, D. V. Steidl)

A sample of the solid thermal decomposition product of plutonium hexafluoride was fluorinated under conditions comparable to

*X-ray determinations performed by D. S. Flikkema and B. S. Tani of the Analytical Group.

those used in a previous study on samples of plutonium tetrafluoride from various sources (ANL-5875). The experimental methods used in these experiments have been reported previously (ANL-5875).

Table 7

BULK DENSITIES OF PLUTONIUM
TETRAFLUORIDE SAMPLES
FROM SEVERAL SOURCES

Source	Bulk Density ^a (g/cc)
PuF ₄ - Rocky Flats	1.29
PuF ₄ from reaction of BrF ₃ with U-Pu alloy	0.88 ₅
Product from thermal decomposition of PuF ₆	2.7 ₆

^aAll density values were determined experimentally under comparable conditions.

The sample of decomposition product was a composite from several plutonium hexafluoride decomposition experiments at 300 C. The major portion of the material had been exposed to a temperature of 300 C for three to four hours. The solid was dark brick red in color, and it had a considerably higher bulk density than samples of plutonium tetrafluoride from other sources (Table 7).

The fluorination reactions were conducted in a flow system. The variables measured were initial and final sample weights, temperature, time, and fluorine flow rate. The rates were calculated by the method described in the uranium trioxide fluorination experiments. The results of the experiments are presented in Table 8. In Table 9 these data are compared with those obtained previously from other samples of plutonium tetrafluoride.

The data obtained from this series of experiments show a rather large scatter. This is believed to arise from the relatively large error possible in determining the surface area exposed to the fluorine. In general, the fluorination rate of the plutonium hexafluoride decomposition product is approximately the same as for the Rocky Flats plutonium tetrafluoride. A rough approximation of the activation energy of the decomposition product fluorination reaction was obtained from the data at three temperatures. The resulting value is 11 kcal/mole, in reasonable agreement with the activation energies obtained for other samples of plutonium tetrafluoride.

Table 8

FLUORINATION RATES OF THE SOLID
THERMAL DECOMPOSITION
PRODUCT OF PLUTONIUM
HEXAFLUORIDE

Fluorine Pressure:	1 atm, 100% fluorine
Fluorine Flow Rate:	60 to 110 ml/min; constant for each experiment
Source of Decomposition Product:	See Text
Bulk Density of Solid:	2.76 g/cc

Exp	Initial Weight (mg)	Final Weight (mg)	Temp (C)	Time (min)	Rate [mg PuF ₄ /(hr)(sq cm)]
107	110.6	108.7	200	60	1.23
112	158.6	155.6	200	120	0.87
108	92.8	81.7	300	20	23.3
111	100.2	90.1	300	30	13.7
109	105.0	86.0	375	20	38.8
110	95.4	74.1	375	20	45.3

Table 9

COMPARATIVE FLUORINATION RATES OF PLUTONIUM
TETRAFLUORIDE FROM SEVERAL SOURCES

Source	Rate [mg PuF ₄ /(hr)(sq cm)]			ΔE^* (kcal/mole)
	200 C	300 C	375 C	
Rocky Flats ^a	1.52	15.4	53.8	12.5
Los Alamos ^a	3.07	26.8	86.7	11.7
Dissolution Residue ^{a,b}	17.1	140	328	10.4
Decomposition Product ^c	1.23 0.87	23.3 13.7	38.8 45.3	11

^aCalculated from previous data (ANL-5875).

^bFrom dissolution of U-Pu alloy in bromine trifluoride.

^cThermal decomposition of plutonium hexafluoride at 300 C.

2. The Reaction of Fluorine with Nickel Surfaces (R. K. Steunenberg, L. Seiden,* H. E. Griffin)

The consumption of fluorine by nickel surfaces is of practical and fundamental interest in fluoride volatilization studies, since it is the basis of corrosion and prefluorination phenomena in nickel systems containing reactive fluorides. Experiments have been performed on the consumption of fluorine by a heated nickel vessel, using the decrease in pressure to follow the reaction as a function of time.

The apparatus used for the determinations is shown in Figure 5. A welded "A"-nickel vessel having a volume of 129 ml and an internal surface area of approximately 200 sq cm

FIGURE 5
APPARATUS FOR FLUORINE
CONSUMPTION EXPERIMENTS

was suspended in a two-inch tube furnace. A new vessel was used for each experiment. The furnace temperature was regulated by a Wheelco controller and the vessel temperature was measured with a thermocouple inserted into a central well in the vessel. The remainder of the system, which had a volume of 100 ml, was at room temperature. A Booth-Cromer pressure transmitter¹³ in conjunction with a mercury manometer was used to measure the pressure in the system.

In order to perform an experiment, the vessel was first cleaned with 6.5 M nitric acid for about two minutes, rinsed with distilled water, and dried with acetone. It was then attached to the apparatus and evacuated. The manifold portion of the system was prefluorinated, but the vessel and connecting tubing were not. The vessel was heated to the temperature of the experiment and fluorine of greater than 99 per cent purity was admitted to give a starting pressure of about 500 mm. The fluorine consumption was then followed by observing the pressure with the mercury manometer. The times of exposure were between 50 and 200 hours.

This technique was found to be highly sensitive and reasonably reproducible in a series of experiments at 300 C. It is recognized, however, that further refinements of the technique and apparatus would be desirable. The nature of the nickel surface within the vessel was not well-defined, the manifold portion of the system was not temperature controlled and the fluorine pressure was allowed to decrease as the reaction progressed. Therefore, in order to check these data, it is felt that independent determinations of the rate by another method, such as weight gain measurements, would be useful.

*ANL Trainee, ISNSE

In order to compute the quantity of fluorine consumed from the pressure decrease, the ideal gas law was used, assuming the cool portion of the apparatus to be at room temperature and the hot portion to be at the vessel temperature. This type of calculation was found to be reliable by testing it with nitrogen and with helium in the system.

The experimental data are represented by the curves in Figure 6, which indicate the relative amounts of fluorine consumed at 300,

400, 500, and 600 C as a function of time. Attempts were made to fit the data to the various rate laws characteristic of metal oxidation processes. At the two lower temperatures a logarithmic rate law appeared to hold, but, as the temperature was raised, the tendency was toward a parabolic behavior. Thus, the rate, after the initial rapid reaction, shows less tendency to level off at the higher temperatures. Due to the changing rate-law behavior of the reaction, a valid activation energy cannot be calculated. It can be estimated roughly, however, from the slopes of logarithmic curves approximating the initial

stages of the reaction, giving a value in the vicinity of 5 to 10 kcal/mole. The change in rate-law behavior with temperature is believed to be reasonable; a similar effect has been noted in work on the oxidation of nickel.¹⁸

The fact that the rate of fluorine consumption by nickel varies with the time of exposure suggests that much of the previous corrosion work reported on this reaction should be considered in this light. Since most of the previous data were based on observations for a single given time period, they probably tend to be pessimistic, assuming that film cracking or other such effects do not become important in very long periods of exposure.

B. Pilot Plant Studies (W. J. Mecham)

In the fused fluoride volatility process for the recovery of enriched uranium from zirconium-alloy reactor fuels, two high-temperature steps are involved. The fuel alloy is dissolved by hydrofluorination in a molten sodium fluoride-zirconium fluoride mixture, and the uranium hexafluoride is then volatilized from the fused salt by sparging with fluorine or an equivalent fluorinating agent. In both steps of this process corrosion is

¹⁸Kubachewski, O. and Hopkins, B. E., "Oxidation of Metals and Alloys," Academic Press, Inc., New York, (1953).

the most severe practical problem. Graphite is a promising material of construction for the hydrofluorination step. A graphite dissolver designed and built by Horizons, Inc. is being installed for pilot plant tests.

In the fluorination step, corrosion is more severe. Approach to this problem is being made along the lines of (1) corrosion tests (described on pages 48 to 52), and (2) development of alternate fluorinator designs in which corrosive conditions are minimized, i.e., no fused salt-metal contact. Two such design concepts are being studied: frozen-wall containment and dropwise fluorination.

Distillation of uranium hexafluoride has long been considered a promising means of decontamination and purification. Currently some small-scale distillation tests and a vapor-liquid equilibrium study have been made.

1. Installation of Graphite Dissolver
(R. W. Kessie, W. Pehl, W. Mecham)

Work is continuing on the fabrication and installation of the graphite dissolver-hydrofluorinator for pilot-plant tests of the dissolution of zirconium-uranium fuel elements in a fused zirconium fluoride-sodium fluoride mixture. Most of the panel board and services are installed. The new internal graphite parts for the dissolver are being fitted. Some new auxiliary components being fabricated are scheduled for completion about November 1.

2. Dropwise Fluorination
(J. Lunsford,* T. McIlrath,** R. C. Liimatainen)

Fluorination of fused salt by spraying the melt into a fluorine atmosphere is a possible means of avoiding fused salt-metal contact under fluorinating conditions. An evaluation study of this alternate processing scheme is under way.

A drop fluorination process is presented conceptually in Figure 7. Salt is held molten above a spray nozzle and forced through the nozzle by gas pressure. The walls of the vessel are at a temperature below the melting point of the salt in order that molten salt will not contact the wall. The salt and, possibly, the fluorine are heated above the melting point of the salt in order to lengthen the contact time before solidification. Solid salt particles are collected from the bottom of the reaction vessel and from a solids separator in the off-gas line. As shown, the uranium hexafluoride is collected in a cold trap. Both fluorine and salt may be recirculated.

*Research Associate from Massachusetts Institute of Technology.

**Student Aide from Michigan State University.

FIGURE 7
DROPWISE FLUORINATOR PROCESS CONCEPT

In such a process the steps involved in removal of uranium from the drop are (1) diffusion of uranium tetrafluoride to the surface of the drop, (2) reaction of the uranium tetrafluoride with fluorine to form uranium hexafluoride, and (3) diffusion of uranium hexafluoride into the bulk of the gas. The time available for material transfer is that in which the drop is molten and in contact with fluorine. For removal efficiencies of the order of 99 per cent, required times in the range 0.01 to 10 sec have been estimated for reasonable drop sizes, i.e., 5 to 1000 microns. Smaller drops favor faster mass transfer. Cooling rate and speed of droplets are important variables which dictate equipment size. The manner of spraying determines drop size and speed.

Tests were made on the spraying of molten salt through nozzles. A single-fluid nozzle was employed for initial tests because of its simplicity of operation.

A 70-degree hollow cone spray nozzle (0.028-inch orifice, Spraying Systems Co. No. 1/4 LN2) was used in a preliminary spray test with the sodium fluoride-zirconium fluoride salt. The molten salt was forced through the nozzle by helium pressure of about 60 psig. A fine, uniform spray was obtained. Droplets, which solidified in flight in this spray test, were shown photographically to be fairly uniform spherical particles, with an average particle size of about 60 microns in a range of about 20 to 140 microns.

Work is continuing on refining calculations of the effect of various parameters on process efficiencies. Also equipment has been assembled to serve as a spray chamber for exploratory fluorination tests.

3. Frozen-Wall Containment (R. W. Kessie, J. D. Gabor)

A molten salt can be contained in its own solid phase by providing internal heating while cooling the outer wall of the vessel; thereby

direct contact of molten salt and a metal container wall can be avoided. A study is under way to investigate the conditions for such stable, controlled frozen walls and to develop practical designs of process equipment using a frozen wall.

Methods of heating under consideration include:

1. electrical resistance heating of an internal metal element in contact with the molten salt;
2. passage of alternating electric current through the molten salt itself, with metal electrodes being required to bring in power; and
3. indirect heating of the molten salt by a radio-frequency coil not in contact with molten salt.

Of these, the last holds the promise of complete elimination of fused salt-metal contact.

Preliminary tests are in progress with a low-melting salt mixture as a stand-in. Process calculations have been made, and full-scale equipment for high-temperature tests is under design. These test vessels will have provision for measuring temperature and locating frozen salt areas.

The fused salt has an electrical resistivity of the order of 1 ohm-cm, while the solid-phase resistivity is several orders of magnitude higher. Therefore, much higher eddy currents will be induced in the liquid phase and relatively little heat will be generated in the solid phase. Calculations indicate that frequencies of 400 kilocycles or higher are capable of efficient heat input to a fused salt charge of approximately six inches in diameter. This has been confirmed by induction heater tests at 10, 350, and 30,000 kilocycles. In these preliminary tests sulfuric acid or low-melting nitrate salts were used; these materials have values of resistivity close to the sodium fluoride-zirconium fluoride process salt.

Maintenance of a stable frozen wall in fused salt by induction heating has been demonstrated on a small scale. In this test a two-inch diameter, five-inch high nitrate salt charge was heated in a water-jacketed glass vessel. An external seven-turn coil coupled to a 30-megacycle radio-frequency generator was used to provide power. Gas sparging made possible a thin, nearly uniform frozen wall on both sides and bottom. However, the frozen wall could also be maintained without sparging by a suitable coil location near the bottom of the charge.

Tests on a larger scale and with the sodium fluoride-zirconium fluoride salt are planned.

4. Draft-Tube Effectiveness in Sparging Tests (J. D. Gabor, C. V. Gorman)

In fluorination of fused salt by sparging, both gas-liquid contacting and liquid mixing are involved. It has been considered here and elsewhere that a draft tube might have the desirable effect of improving liquid circulation by gas-lift action. Tests with a mock-up system were made to compare quantitatively the sparging effectiveness with and without a draft tube for removal of a volatile component dissolved in a liquid. Elimination of the draft tube has the advantage of simplicity of construction.

A mock-up system of carbon dioxide and water was used in current tests. The carbon dioxide was dissolved in water and stripped out with air. The concentration of the carbon dioxide was reduced from approximately 0.04 mole per cent to 0.005 mole per cent, compared to an expected change in the uranium hexafluoride composition in the fluorinator of about 0.3 mole per cent to 0.003 mole per cent.

A six-inch ID glass column simulated the fluorinating vessel, and a 1/4-inch pipe nipple was used as a sparge nozzle. The water level was maintained at approximately three feet. Two draft tubes, two and four inches in diameter, respectively, and 18 inches long, were tested. Samples of the solution were taken through a 1/4-inch stainless steel tube tapped into the bottom of the column and extending 18 inches above the bottom.

The concentration of the carbon dioxide was determined by pipetting a sample of the carbon dioxide solution in a solution 0.1 N in sodium hydroxide and barium chloride. The sodium hydroxide-barium chloride solution was then titrated against hydrochloric acid. The electrical conductivity of the solution was also measured as a qualitative indication of the amount of carbon dioxide in solution.

The data obtained are given in Table 10. The effectiveness of sparging is expressed in terms of the mass-transfer coefficient, k_{La} . Ninety-five per cent confidence limits were placed on the average values for k_{La} . A pooled variance was used to estimate the confidence limits.

These data indicate that increasing the draft-tube diameter/vessel diameter ratio increases the reaction efficiency. A possible explanation for this behavior is that the draft tube tends to confine the sparge gas bubbles and limits the contact of the fluid with the gas. The data also show that operation without a draft tube gives the best k_{La} values.

On the basis of improving contacting efficiency the draft tube does not appear to be desirable. However, a draft tube might have other uses. For example, it might serve as a means of protecting other components in the fluorinator from direct impingement of the fluorine sparge. For frozen wall designs, it is probably desirable to eliminate the draft tube.

Table 10

COMPARISON OF MASS-TRANSFER COEFFICIENTS FOR
VARIOUS DRAFT-TUBE CONFIGURATIONS

(Test on removal of CO₂ from water by air sparge in a
6-inch diameter vessel. Length of sparge: 2 minutes)

Sparge Air Rate (cu ft/min)	Draft Tube Diam (in.)	Mass-Transfer Rate = $k_L a$ (avg) (moles/min)
0.53	2	0.182 ± 0.027
	4	0.227 ± 0.025
	no draft tube	0.236 ± 0.025
1.10	2	0.340 ± 0.043
	4	0.420 ± 0.043
	no draft tube	0.419 ± 0.027

5. Vapor-Liquid Equilibrium Study
(R. C. Liimatainen)

Work on the vapor-liquid equilibrium of the system uranium hexafluoride-bromine pentafluoride is continuing. Data on the 70 C isotherm, now virtually complete, show small positive deviations from ideality over most of the range. In the experiments the addition of small amounts of fluorine to the system has been found necessary to prevent appearance of a red color, indicating bromine formation. A check of the bromine pentafluoride-rich end of the diagram at 70 C and determination of the 90 C isotherm are in progress.

C. Corrosion Studies

(L. Hays, R. Breyné, W. Seefeldt)

Further corrosion data are reported on the relative behavior of nickel and several nickel alloys in fluorinated sodium fluoride-zirconium fluoride at 600 C. These data apply to both the fluoride volatility program and the LMFR program. Nickel-molybdenum alloys (Hastelloy B* and INOR-1*) show relative immunity to intergranular attack when compared to "L" nickel and "D" nickel* in liquid phase and interface exposure. Dimensional changes are about comparable in the four materials tested.

It has been observed in recent tests that Hastelloy B and "L" nickel coupons suffer severe attack in the vapor phase. Two "A" nickel liners, a sparger, and a thermocouple well used in conjunction with these tests were

*Typical Analyses: Hastelloy B: 28 Mo, 5 Fe, 1 Mn, 1 Si, Balance Nickel
INOR-1: 20 Mo, Balance Nickel
"D" Nickel: 4.5 Mn, Balance Nickel

examined to determine if "A" nickel under heat transfer conditions is also sensitive to this type of attack. The result was positive. This was further confirmed from a corrosion rod specimen from a fluidized bed fluorinator.

1. Comparative Tests of "L" Nickel, "D" Nickel, Hastelloy B, and INOR-1

The above metals were tested partially immersed in equimolar sodium fluoride-zirconium fluoride at 600 C through which fluorine was bubbled. Test parameters included time and fluorine rate. Corrosion assessment included weight loss, dimensional change, and intergranular attack. Further details of the test and evaluation methods were described in ANL-5896, page 53.

Hastelloy B has a higher molybdenum content than INOR-1 and examination of a phase diagram reveals that an equilibrium alloy of Hastelloy B would contain a second phase, while INOR-1 would not. As a result, Hastelloy B is usually used in the solution heat-treated state. However, prolonged exposure at elevated temperatures, as this application would involve, results in precipitation of the second phase, with subsequent loss of ductility (known as age hardening). This does not occur with INOR-1. On this basis INOR-1 would be potentially the more useful material. As supplies of INOR-1 were limited, a larger number of tests were conducted with Hastelloy B since it was expected that in greater part the corrosion behavior would be similar.

"L" nickel serves as the reference material for these tests, as it was the original material considered useful, and the one considered most noble in a fluorine environment. "D" nickel was included because its manganese content should make it less sensitive to intergranular attack by sulfur-containing impurities.

Two of the metals - Hastelloy B and "L" nickel - were tested for three different exposure times and two fluorine flow rates. The other two metals - INOR-1 and "D" nickel - were tested for one exposure time and one fluorine rate. Table 11 includes data from the latter tests, while Tables 12 and 13 include all the data obtained with the various parameters for the Hastelloy B and "L" nickel tests.

The most significant conclusion to be derived from the data is the high resistance that the nickel-molybdenum alloys have to subsurface or intergranular attack. Table 11 shows that for liquid phase and interface exposure, no subsurface attack was observed in INOR-1 in 63 hours of fluorine exposure, while a maximum of 0.7 mil was found in Hastelloy B. These numbers are substantially lower than those obtained with "L" and "D" nickel (16.8 and 5.3 mils, respectively). Of the four materials, it appears that INOR-1 is also superior relative to dimensional change. Its superiority

Table 11

COMPARATIVE CORROSION OF SEVERAL NICKEL ALLOYS
IN FLUORINATED FUSED FLUORIDES

Conditions: Coupons wired in form of draft tube and partially immersed in NaF-ZrF₄ at 600 C; fluorine introduced centrally below melt level; containing vessel and gas entrance tube made of "A" nickel.

Exposure Time: 63 hours fluorine sparge,
153 hours helium sparge.

Fluorine Flow Rate: 10 g/hr

Corrosion Observed, mils

Alloy		Liquid Phase		Interface	Vapor Phase	
		Typical	Max		Typical	Max
"L" Nickel	(D) ^a	2.0	2.6	3.2	1.1	1.5
	(S) ^a	5.8	6.0	16.8	1.4	2.9
	(T) ^a	7.8	8.6	20.0	2.5	4.4
"D" Nickel	(D)	4.0	5.0	4.0	3.4	5.7
	(S) ^b	3.6	4.8	5.3	1.8	3.5
	(T)	7.5	8.1	7.5	4.6	7.2
Hastelloy B	(D)	1.2	1.8	2.3	0.7	1.8
	(S)	0.3	0.7	0.5	0.5	1.0
	(T)	1.5	2.5	2.8	1.2	3.8
INOR-1	(D)	0.3	0.4	2.8	1.4	3.2
	(S)	0	0	0	0.1	0.2
	(T)	0.3	0.4	2.8	1.5	3.2

^a(D) = dimensional change

(S) = subsurface attack

(T) = total attack = (D) + (S)

^bThe subsurface attack in the case of "D" nickel was the formation of subsurface voids; no intergranular attack observed.

in this respect is marked in the liquid phase, less so at the interface. However, even at the interface, the total attack of INOR-1 is a factor of seven less than that of "L" nickel and nearly a factor of three less than "D" nickel. The comparisons above are also valid for Hastelloy B, but to a somewhat lesser degree.

Table 12

CORROSION OF "L" NICKEL AND HASTELLOY B IN FLUORINATED FUSED
FLUORIDE: LIQUID PHASE AND INTERFACE ATTACK

Conditions: Coupons wired in form of draft tube and partially immersed in NaF-ZrF₄ at 600 C; fluorine introduced centrally below melt level; containing vessel and gas entrance tube made of "A" nickel.

Location	Fluorine Rate (g/hr)	Exposure Time ^a (hr)	Corrosion Observed, mils					
			Dimensional Change		Intergranular Attack		Total Attack	
			Hastelloy B	"L" Nickel	Hastelloy B	"L" Nickel	Hastelloy B	"L" Nickel
Liquid Phase, Typical Interface	5 ↓	7	0.4	0.4	0.5	2.4	0.8	2.6
		21	0.4	0.7	0.2	3.0	0.6	3.5
		63	0.6	1.5	0.2	8.5	0.8	9.7
		7	0.6	0.9	0.8	3.6	1.4	4.5
		21	0.6	1.1	0.5	3.0	1.1	4.1
		63	1.3	4.9	0.4	10.8	1.7	15.7
Liquid Phase, Typical Interface	10 ↓	7	0.2	0.5	0.2	1.4	0.4	1.9
		21	0.4	0.6	0.2	2.0	0.6	2.6
		63	1.2	2.0	0.3	5.8	1.5	7.8
		7	0.6	1.3	0.2	3.5	0.8	4.5
		21	1.6	0.9	0.2	3.1	1.8	4.0
		63	2.3	3.2	0.5	16.8	2.8	20.0

^aExposure times listed include fluorine sparge only; for every 7 hours of fluorine sparge, there were 17 hours of helium sparge.

Table 13

CORROSION OF "L" NICKEL AND HASTELLOY B IN FLUORINATED FUSED
FLUORIDE: MAXIMUM VAPOR PHASE ATTACK

Conditions: Coupons wired in form of draft tube and partially immersed in NaF-ZrF₄ at 600 C; fluorine introduced centrally below melt level; containing vessel and gas entrance tube made of "A" nickel.

Fluorine Rate (g/hr)	Exposure Time ^a (hr)	Corrosion Observed, mils					
		Dimensional Change		Intergranular Attack		Total Attack	
		Hastelloy B	"L" Nickel	Hastelloy B	"L" Nickel	Hastelloy B	"L" Nickel
5	7	0.5	0.7	1.2	0.7	1.7	2.7
	21	1.1	0.8	4.0	1.9	5.1	2.6
	63	1.8	1.9	1.6	4.6	3.4	5.6
10	7	0.3	0.5	0.7	0.5	1.0	3.1
	21	1.3	0.9	0.5	2.2	1.8	3.0
	63	1.8	1.5	1.0	2.9	3.8	4.4

^aExposure times listed include fluorine sparge only; for every 7 hours of fluorine sparge, there were 17 hours of helium sparge.

From these data one can conclude that INOR-1 would be the most promising material of those tested for the construction of a conventional fluorinator with its greatest advantage being relative immunity to subsurface attack.

2. Vapor Phase Corrosion of Test Components

During the course of the tests described in Section 1, it was noted that both "L" nickel and Hastelloy B coupons suffered high attack in the vapor phase. Figure 8 is a typical thickness contour of an "L" nickel coupon.

FIGURE 8
TYPICAL THICKNESS CONTOUR OF "L" NICKEL
SUBJECTED TO FLUORINATED SODIUM FLUORIDE -
ZIRCONIUM FLUORIDE AT 600 C
Exposure Time : 63 hours F_2 sparge
Fluorine Rate : 10 g/hr

In the past no such effect has been observed in nickel. However, previous observations were made on liners (containment vessels) through which heat was transferred from external heating elements, while coupons used in the current tests did not transfer heat. The "A" nickel liner, thermocouple well, and sparge tube used in conjunction with the coupon tests were examined to determine whether they had suffered any vapor phase attack. Evaluation included both dimensional change and intergranular attack. The results are similar to those shown in Figure 8.

All three test components showed a minimum amount of corrosion somewhat above the interface, with larger amounts of corrosion occurring some distance above this minimum in the vapor phase. In great part this attack was less than that observed in the liquid phase or at the interface. However, this confirms that in "A" nickel there is a region of more aggressive attack in the vapor phase that may be important in a modified process or in equipment utilizing frozen-wall techniques.

3. Miscellaneous Tests

Boron nitride was exposed to fluorinated sodium fluoride-zirconium fluoride at 600 C under partially immersed conditions. The material was reported to have reasonable resistance to fused salts and chlorine up to 704 C (1300 F). After six hours the boron nitride had completely dissolved.

A sample of nickel aluminide was also exposed to fluorinated melt. Photomicrographs taken of the material before exposure showed high porosity. The sample did not retain its physical integrity due to the high porosity. The test was not considered conclusive.

II. LIQUID METAL FUEL REPROCESSING

(J. Fischer)

Laboratory work to demonstrate the practicality of the fused fluoride volatility process for the LMFR fuel is being continued. Attention is being given to experiments which will establish the mechanism and conditions for the removal of cerium (representative of the rare earths), uranium and zirconium from bismuth by extraction with molten mixtures of zirconium fluoride and sodium fluoride.

The rapid extraction of uranium from bismuth, very low in magnesium concentration, has been quantitatively demonstrated. Equilibration experiments have been performed in which alloys of uranium in bismuth (simulating the concentration of uranium in the LMFR fuel) have been contacted with the molten fluoride salt* at 600 C. The uranium concentrations have been lowered to values lower than the blank (apparent) uranium values obtained for pure bismuth equilibrated with the fused salt.

Magnesium, which will be present as an antioxidant in the LMFR fuel, was shown to be incapable of reducing uranium tetrafluoride to uranium and causing its back extraction into bismuth.

Extraction of cerium from bismuth, low in magnesium concentration, by the molten fluoride salt has also been accomplished. Good extraction factors are obtained in short contact times.

Preliminary information, based on autoradiographic tests, indicates that radioactive zirconium can be extracted from bismuth with the molten fluoride salt.

The partial extraction of uranium and radioactive ruthenium from bismuth with zinc has been demonstrated. The extraction of cerium from bismuth with zinc has been shown not to occur.

Bismuth pentafluoride has been prepared by the direct reaction of fluorine with bismuth. The stoichiometry of the compound has been approximately established by determining the approximate amount of fluorine which has reacted with a known weight of bismuth. The crude bismuth pentafluoride can be purified by sublimation.

*The sodium fluoride - zirconium fluoride mixture will hereafter be referred to as the fluoride salt.

A. Extraction of Uranium and Fission Products from Bismuth
(M. Adams, T. Gerding, J. Stockbar, H. Tyler)

1. Procedures Used in Extraction Experiments

In the initial stage of the fused fluoride volatility process for the LMFR fuel, described in ANL-5820, page 35, the FPS group of fission products,* magnesium and uranium may be extracted from the LMFR fuel with the molten fluoride salt, saturated with hydrogen fluoride at 600 C. Extraction experiments have been performed that indicate that uranium and cerium can be extracted from bismuth with the fused salt without the use of hydrogen fluoride.

Two types of uranium extraction experiments have been made. The first type, which will be referred to as a "static experiment," is one in which a uranium-bismuth alloy is contacted without any agitation with molten fluoride salt (55 mole per cent sodium fluoride and 45 mole per cent zirconium fluoride) at 600 C. A second type, which will be referred to as a "shaking experiment," was performed in a rocking furnace which tilts through an arc of forty degrees about a horizontal plane at one cycle per minute.

In the "static experiments" the liquid metal and salt phases were contained in molybdenum crucibles inside a resistance-heated steel furnace. For the shaking experiments cylindrical graphite containers were used. They were degassed in an induction-heated furnace under high vacuum at temperatures higher than 1300 C.

The sample was loaded into a graphite** container in a dry box containing an argon atmosphere, and the container was then sealed with a graphite screw cap. It was then placed in a secondary, cylindrical, copper container. Before equilibrations of salt and metal were made, in both types of experiment, the samples and containers were degassed using a high-vacuum, oil diffusion pump system. An atmosphere of high-purity argon, which had passed through Linde "Molecular Sieves," was admitted to each container before equilibrations were made.

An analysis of the salt mixture, obtained from the Kawecki Company is given in Table 14. The salt was dried and freed of any trace of hydrogen fluoride by evacuation of the salt while in the molten state. An oxygen determination, described in ANL-5896, page 49, indicated there was no detectable amount (less than 0.05 weight percent) of oxygen containing compound in the salt.

*That group of fission products capable of being extracted by the fluoride salt, mainly the rare earths.

**The use of 446 stainless steel as a container material was discontinued when high uranium losses were obtained for alloys melted in 446 stainless steel containers.

Table 14

ANALYSIS OF SODIUM FLUORIDE - ZIRCONIUM
FLUORIDE FUSED SALT^a

	Weight Per Cent		Mole Per Cent
	Experimental	Calculated	
Sodium	13.2	-	-
Zirconium	41.3	-	-
Fluorine	45.3	-	-
Sodium Fluoride	-	24.0	55
Zirconium Fluoride	-	75.7	45
Total Fluorine	-	45.3	-
Hydrogen Fluoride	<<0.1	-	-

^aObtained from Kawecki Chemical Company.

The uranium-bismuth alloy used in Experiments 1365, 1161, 1139, described in Table 15, was a ground composite alloy from which three representative samples were taken and analyzed in duplicate with an average deviation of ± 7 per cent. Alloys used in making up the composite alloy were prepared in alundum crucibles. Preparation of the alloys and the autoradiographic technique used to determine the homogeneity of the alloys used in all the other experiments were described in ANL-5896, page 43. Small amounts of magnesium were used in the preparation of the alloys, but most of the magnesium was lost by volatilization or reaction with the container walls.

Table 15

EXTRACTION OF URANIUM FROM BISMUTH WITH SODIUM FLUORIDE - ZIRCONIUM FLUORIDE

Metal: Bismuth-Uranium Alloy^a
Salt: Sodium Fluoride-Zirconium Fluoride^b
Temperature: 600 C

Exp No.	Type Exp	Contact Time (min)	Wt of Bismuth (g)	Wt of Salt (g)	Uranium in Bismuth before Extraction (ppm)	Uranium in Bismuth after Extraction (ppm)		Uranium in Salt after Extraction (ppm)	Uranium Recovered in Salt (per cent)
						Uncorrected	Corrected ^e		
1365	Static ^c	60	90	89	1015 $\pm$ 70 ^f	3	0	1300	127
1161	Static ^c	10	94	100	1015	2	0	1100	116
1139	Shaking ^d	5	50	15	1015	24	9	4500	133
1174	Shaking ^d	30	50	15	725 $\pm$ 10 ^g	14	0	3700	156
1177	Shaking ^d	30	50	15	725	14	0	2700	114

^aThe density of the molten metal phase is about three times that of the molten salt phase.

^bSee Table 14 for composition.

^cMolybdenum containers.

^dGraphite containers in rocking furnace

^eBlank value 15 ppm subtracted (pure bismuth equilibrated with fused salt).

^fComposite alloy.

^gAverage deviation of duplicate samples.

2. Uranium Extraction Experiments

Results of the uranium extraction experiments are given in Table 15. Uranium in bismuth was determined polarographically, using the amalgam leach procedure described in ANL-5858, page 127. Uranium in the fused salt was determined fluorophotometrically. An apparent uranium value was obtained in the polarographic determination of uranium in pure bismuth equilibrated with the fluoride salt. The blank value (15 ppm) was due to some small impurity in the metal, salt, or analytical reagents. Corrected uranium concentrations in the original alloy are given as parts per million by weight in Table 15. Both the apparent and corrected concentrations of uranium are given for the extracted bismuth.

In static Experiment 1161 the test sample was raised rapidly to 600 C and then cooled rapidly. The contact time of ten minutes was the interval during which the salt remained molten. Contact times for the other experiments were for the intervals during which the samples were at 600 ± 25 C.

The per cent uranium extracted is based on the corrected uranium concentrations in the metal before and after extraction. The per cent uranium recovered in the salt may be accurate to ± 25 per cent, due to a corresponding accuracy in the fluorophotometric analysis of the uranium in the fused salt. However, it clearly indicates that the uranium is extracted by the salt and not otherwise lost.

It can be concluded from the results that uranium can be rapidly and completely extracted from bismuth by the molten fluoride salt at 600 C in the absence of hydrogen fluoride.

Recent work at Brookhaven National Laboratory has shown that a high concentration of magnesium (ca 2000 ppm) is required to prevent the oxidation of uranium in a molten bismuth solution in the presence of air. Concentrations of magnesium in the fuel of 2000 ppm or higher may be used in the LMFR fuel as an antioxidant. Future experiments will be made to determine the effect of magnesium on the extent and rate of uranium extraction from bismuth with the fluoride salt. Attempts will be made to determine the mechanism for the oxidation of the uranium. Experiments will be done to determine to what extent the salt can be reused to extract uranium from the fuel without hydrofluorination of the salt.

3. Effect of Magnesium on the Reduction of Uranium Tetrafluoride in the Fluoride Salt

The ability to reduce uranium tetrafluoride in the molten fluoride melt was investigated to determine if magnesium present in the concentration of 2000 ppm in the bismuth would be capable of causing the back extraction of uranium into the bismuth phase.

Shaking experiments were performed in which the magnesium and bismuth were equilibrated (as in the uranium extraction experiments) with fused salt containing uranium tetrafluoride. The results are shown in Table 16. In Experiments 1163 and 1164 approximately 80 times the magnesium concentration in the LMFR fuel was used, while in Experiments 1192 and 1194 the concentration of magnesium in the bismuth was 2000 ppm. In Experiment 1164 the uranium initially present in the salt phase was that which had previously been extracted from a uranium-bismuth alloy, while in the other experiments the uranium had been added to the fluoride salt as uranium tetrafluoride.

Table 16

REDUCTION EFFECT OF MAGNESIUM ON URANIUM TETRAFLUORIDE IN
MOLTEN SODIUM FLUORIDE - ZIRCONIUM FLUORIDE

Exp No.	Temp (C)	Contact Time ^a (hr)	Weight Bismuth (g)	Weight Salt (g)	Weight Magnesium Added (g)	Weight Uranium in Salt (mg)	Uranium in Bismuth after Contact ^b (ppm)
1163	550	2	60	20	10.0	45.5 ^c	38
1164	590	6	60	20	10.0	ca. 20 ^d	0
1192	550	2	60	20	0.12	45.5 ^c	0
1194	550	2	60	20	0.12	45.5 ^c	0

^aShaking experiment - graphite container.

^bBlank value 15 ppm subtracted.

^cAdded as uranium tetrafluoride.

^dSample of salt from an extraction of uranium from bismuth.

Thus, the magnesium present in an amount approximating its concentration in the LMFR fuel is not capable of reducing uranium tetrafluoride to uranium while dissolved in the molten fluoride salt. It therefore seems reasonable to assume that the magnesium in the LMFR fuel will not prevent the oxidation and extraction of uranium by the fluoride salt. However, the rate at which uranium is extracted by the fused salt may be decreased by the magnesium, which itself is most likely oxidized and extracted by the salt. Experiments to determine the relative rates of extraction of magnesium and uranium are in progress.

4. Cerium Extraction Experiments

Extraction of cerium from bismuth with the fluoride fused salt has been studied in shaking experiments in the same manner as the uranium extractions. Uranium-irradiated cerium alloys were contacted with fused

salt in graphite containers in the rocking furnace. Cerium was irradiated in CP-5 and the uranium-cerium alloys were prepared and checked for homogeneity autoradiographically as described in ANL-5896, page 43.

Data for the cerium extraction experiments are given in Table 17. In the first three experiments the cerium concentration in the bismuth was 1000 ppm, based on the weight of the cerium added. The concentration in the alloy for Experiment 1170 was 42 ppm, which was calculated from the activity of the alloy and the specific activity of the irradiated cerium counted at the same time. The latter concentration of cerium approximates in order of magnitude the fission product build-up to be expected in the LMFR fuel. The cerium activity was determined from the gamma activity counted with a well-type scintillation counter. Beta activity in the sample was attenuated by the use of aluminum between the sample and the crystal.

Table 17

EXTRACTION OF CERIUM FROM BISMUTH WITH SODIUM
FLUORIDE - ZIRCONIUM FLUORIDE

Metal: Bismuth-cerium alloy containing irradiated cerium - 50 g
Salt: Sodium fluoride - zirconium fluoride^a - 15 g
Container: Graphite

Exp No.	Temp (C)	Time ^b (min)	Activity of Original Alloy (cpm/g)	Conc of Cerium (ppm)	Activity of Fused Salt after Extraction (cpm/g)	Activity of Bismuth after Extraction (cpm/g)	Extraction Factor ^e
1366	600	180	2.87×10^3	10^{3c}	1.6×10^4	56	51
1159	600	30	2.52×10^3	10^{3c}	1.0×10^4	3	8×10^2
1156	580	5	2.52×10^3	10^{3c}	6.18×10^3	84	30
1170	600	5	5.10×10^3	42 ^d	2.44×10^4	1.62×10^2	31

^aSee Table 14 for composition.

^bTime in rocking furnace at experiment temperature.

^cBased on cerium added to alloy.

^dCalculated from activity of the cerium.

^e $\frac{\text{Activity of bismuth before extraction/gram bismuth}}{\text{Activity of bismuth after extraction/gram bismuth}}$

The results indicate that cerium can be rapidly extracted from bismuth with the molten fluoride salt. Extraction factors given in Table 17 are the ratios of the cerium activity in the bismuth phase before and after extraction. Good material balance is obtained between the activity in the metal phases and the salt phase.

Experiments will be performed in the future to determine the effect of magnesium on the extraction of cerium.

5. Extraction of Zirconium

A preliminary result based on the autoradiograph of an extracted bismuth-irradiated zirconium alloy and the equilibrated salt phase indicates that zirconium can also be extracted from the LMFR fuel with the fluoride salt. The mechanism of extraction, which may entail oxidation of zirconium or exchange of zirconium with the fused salt, is being studied.

6. Extraction of Ruthenium, Uranium, and Cerium with Zinc

Four experiments were made to check on the extraction of ruthenium, uranium, and cerium from bismuth with zinc. Preliminary autoradiographic results were given in ANL-5896, page 46. Analytical data for the experiments are presented in Table 18. Partial extraction of ruthenium and uranium was obtained. Cerium was not extracted by the zinc.

Table 18

EXTRACTION OF BISMUTH ALLOYS WITH ZINC

		Temperature:	500 C			
		Container:	446 SS capsules			
		Weight Bismuth:	45 g			
		Weight Zinc:	5 g			
			Bismuth Activity ^a		Uranium Concentration	
			(cpm/g)		in Bismuth	
		Contact			(ppm)	
Exp No.	Metal Extracted	Time (hr)	Before	After	Before	After
			Extraction	Extraction	Extraction	Extraction
1369	Ru	24	2.16 x 10 ⁴	2.48 x 10 ³	-	-
1372	Ce	19	3.68 x 10 ³	7.27 x 10 ³	-	-
1373	Ce	22	3.68 x 10 ³	7.85 x 10 ³	-	-
1374	U	24	-	-	995	350

^aAnalytical data may be approximate, due to alloy inhomogeneity.

Work on the extraction of the FPN group of fission products will be suspended. The American Smelting and Refining Company, under a Brookhaven National Laboratory subcontract, is doing extensive work on the extraction of ruthenium, palladium, and tellurium from bismuth by zinc slagging, as reported in BNL-506.

B. Bismuth Fluoride Chemistry
(E. Rudzitis and W. Gunther)

The program was originated with the idea that bismuth fluorides might be used as oxidizing agents in the fused fluoride volatility process for the LMFR fuel; it was also realized that in certain phases of the process formation of bismuth fluorides was possible. A literature survey revealed that the information on physical and chemical properties of bismuth fluorides is far from complete. Accordingly it was decided that, concurrently with the process-applied phase of the research, investigations should be made on the more fundamental aspects of bismuth fluoride chemistry. Bismuth is known to form two fluorides - bismuth trifluoride and bismuth pentafluoride. Bismuth trifluoride is quite well known and can be prepared from aqueous solutions. Bismuth pentafluoride has been obtained relatively recently,¹⁹ by passing fluorine over bismuth trifluoride at 500 C; however, no definite identification of the product had been made. Also, except for some qualitative statements, pertaining to pronounced reactivity of the compound, no information of the chemical and physical properties of bismuth pentafluoride is available.

The first portion of the present investigation is devoted to preparation, purification, and identification of bismuth pentafluoride. A method of preparing bismuth pentafluoride by direct fluorination of bismuth in a constant volume system has been developed. Thirty grams of liquid bismuth, in an alumina crucible within a nickel liner, were exposed at 530 to 550 C to a fluorine pressure of 1500 mm. After a short induction period the beginning of the reaction could be observed by a pressure decrease and a temperature increase. After the reaction was initiated the temperature could be reduced to 450 C without interrupting the reaction. In previous experiments it was found that it was difficult to get the reaction started below 530 C. It was also found that a lower reaction temperature was preferable because bismuth trifluoride tends to volatilize at the higher temperature and contaminates the product. The yield of bismuth pentafluoride seems to increase with decreasing temperature. As the reaction proceeded, fluorine was added in such a manner that fluorine pressure in the 1500-cc system regularly varied between 1500 and 1000 mm. The fluorine was absorbed at a rate of approximately 0.1 mole per hour. After the theoretical amount of fluorine necessary to form bismuth pentafluoride was absorbed, the rate of fluorine consumption decreased and the experiment was terminated. Upon opening the liner in a dry box, it was found that the crucible was empty and the reaction product had condensed in the form of white needles on the upper portion of the liner which was cooled. When exposed to air, the substance turned brown immediately, liberating hydrogen fluoride. It reacted violently with water. The crude bismuth pentafluoride can be purified by repeated sublimation in a Pyrex tube at 120 to 150 C without visible attack. Future work will include refining and expanding the experiments on preparation, identification, and properties of bismuth pentafluoride and bismuth trifluoride.

¹⁹Von Wartenberg, H., Z. Anorg. Chem. 240, 337 (1940).

III. FLUIDIZATION STUDIES

Development work on the process for the recovery of uranium from low uranium-high zirconium alloys (ADF process) was continued. The process includes aqueous dissolution, fluid-bed drying and fluid-bed fluorination of the uranium to the hexafluoride (see a process flow diagram in Figure 10, page 69). Runs in the six-inch diameter fluid-bed dryer were made at 300 C using feed solutions containing the equivalent of five and ten weight per cent uranium alloys. The drying unit was also operated successfully at 240 C, thus extending the process operating temperature range to 240 to 450 C. Refractory-grade zirconium oxide and calcium fluoride were compared as starting bed materials. Generally the oxide was more satisfactory. Some particle growth occurred in the bed, but at a rate which did not interfere with operations.

As part of a study to correlate uranium removal during fluorination with species of zirconium fluoride formed at various drying temperatures, identification of fluid-bed dryer products was attempted. X-ray diffraction studies of products prepared from feed solutions containing a fluoride to zirconium mole ratio of ten indicate several polymorphic forms of zirconium tetrafluoride might be formed at 300 C, while zirconyl fluoride is formed at 450 C. A series of ignition tests was made at 450 C on materials dried at 300 C. Both water and hydrofluoric acid were evolved in small and varying amounts.

Fluorinations in the 2½-inch diameter fluid-bed unit succeeded in removing about 99 per cent of the uranium in four hours at 600 C and 12 hours at 500 C from materials prepared in a fluid-bed dryer at 300 C. Equivalent results were achieved on material dried at 240 C. The feed contained the equivalent of five and ten weight per cent uranium alloys. Poor uranium removal was achieved in a run at 500 C on fluid-bed dried material containing precipitated uranium tetrafluoride (3.5 weight per cent alloy equivalent).

Laboratory fluorination studies showed metal additives to uranium-zirconium feed solutions had no inhibiting effect on uranium volatilization. A single laboratory experiment was performed in which 20 moles of carbon per mole of uranium were added to the feed. About 87 per cent of the uranium volatilized, while 96 per cent of the carbon was removed in two hours of fluorination at 600 C.

In the fluid-bed waste calcination process currently under investigation, liquid radioactive wastes are spray injected into a heated fluidized bed of solid particles. During the last quarter, emphasis has been placed on determining the efficacy of a venturi scrubber and a silica gel adsorber in removing ruthenium from the calciner off-gas. A series of runs has been made using ruthenium-106 as tracer in a synthetic feed. The scrubber and absorber removed ruthenium from the off-gas by factors of 500 to 800.

Preliminary experiments have been completed in the radioactive tracer mixing studies carried out in straight and tapered fluidized beds using copper metal powder and granules. The rate of mixing followed the diffusion equation in the straight column but not in the tapered column. A mixing coefficient of 0.005 sq ft/sec, independent of gas velocity, was obtained in the straight column. The rate of mixing was retarded in the tapered bed, although the rate increased with increasing flow rate. The minimum fluidizing velocity is higher in the tapered bed, and slugging and bed expansion are reduced.

A study of the factors influencing particle growth in a fluid-bed calciner was started. Initial experiments were conducted with sodium carbonate solutions using a three-inch diameter column. Microscopic examination of dried particles disclosed no growth rings such as had been observed with products from uranyl nitrate and zirconium fluoride solution calcinations.

Discussions were held this quarter with representatives from Phillips Petroleum Company on fluid-bed calcination of aluminum nitrate waste solutions and processing of uranium-zirconium fuel alloys.

A. Separation of Uranium from Zirconium-Uranium Fuel Alloys

The term "ADF Process" has been selected to designate the general fuel recovery process which involves aqueous dissolution of the fuel, drying of the solution to solids, and subsequent fluorination of the fissile elements. Development work is being carried out on an engineering scale to apply the process to enriched uranium-zirconium fuel alloys of the STR type. Laboratory work is also being done on application of the process to uranium-plutonium fuels (see Section I, page 24). For the zirconium alloys, the process involves dissolution of the alloy in aqueous hydrofluoric acid, followed by conversion of the metal to dry granular solids by spraying the solution into a fluidized bed of granular material. The solids are then fluorinated in a fluid-bed reactor to remove the uranium as the volatile hexafluoride.

Successful operation of the fluid-bed dryer has been achieved in previous work over a temperature range of 300 to 450 C. Preliminary laboratory fluorination studies showed the bulk of the uranium can be readily separated from the dried solids, but quantitative separation is more difficult.

Additional investigations of operating variables were performed in the six-inch diameter fluid-bed dryer while preparing material for fluid-bed fluorination studies. A comparison of refractory grade zirconium oxide and calcium fluoride as starting bed materials was made. In order to extend the operating temperature range of the fluid-bed dryer, a low temperature (240 C) run was conducted. X-ray diffraction study of

the dryer products was continued. The 2.5-inch diameter fluid-bed fluorinator was successfully operated at 500 and 600 C using fluid-bed dryer products. About 99 per cent uranium removal was achieved for materials containing the equivalent of five and ten weight per cent uranium alloys. Laboratory fluorination experiments included studies of the effect on uranium volatilization of fluid-bed drying temperature and of carbon and metal additives to feed solutions.

1. Fluid-Bed Drying

(J. Barghusen, N. Levitz, D. Raue, R. Finley)

a. Operating Conditions

Since the use of calcium fluoride as a starting bed material in earlier runs was suspected of having contributed to caking of the bed, two sets of runs were made using refractory grade zirconium oxide to determine if the use of the more porous oxide, as compared to the crystalline calcium fluoride, would eliminate the tendency for the bed to cake at the outset of the drying runs.

Operating conditions for the series of runs are summarized in Figure 9. The first set of three runs: ZCP-40, 41, and 42, was made at a bed temperature of 300 C and a feed rate of 90 ml/min. The feed contained about 1.5 M zirconium, 0.07 M uranium as uranyl fluoride (equivalent to a 10 weight per cent uranium-zirconium alloy), and a fluoride to zirconium mole ratio of 4.5.

A single run, ZCP-43, was made at a bed temperature of 285 C using a fresh oxide bed and a much lower feed rate, 55 ml/min instead of 90 ml/min, in an attempt to pre-coat the oxide and eliminate particle growth and bed caking which occurred during Runs ZCP-40 and 41. The feed for this run contained no uranium. The final bed from this run was used as a starting bed for the low temperature study, Run ZCP-44 at 240 C. The feed for Run ZCP-44 contained 0.03 M uranium as uranyl fluoride, which is equivalent to a five weight per cent uranium-zirconium alloy. A comparative set of Runs: ZCP-45, 46, and 47, was made with a calcium fluoride starting bed and low feed rate, varying between 43 and 50 ml/min.

All of the fluid-bed dryer runs were made with a fluidizing gas velocity of two feet per second at column conditions. For Runs ZCP-40 to 46 purge air was introduced into the feed line just upstream from the nozzle to maintain a high liquid velocity in the nozzle. The purge air was found desirable in previous runs using slurry feeds, but may not be necessary for the present clear liquid feeds. Use of the purge air in the feed stream was discontinued after Run 46. An atomizing air pressure of 30 psig was used with a 0.040-inch liquid nozzle. This pressure produces a uniform spray pattern for flow rates above 20 ml/min.

FIGURE 9
SUMMARY OF RUNS MADE IN SIX-INCH FLUID BED DRYER

^a Starting bed for these runs was the final bed from the previous run.

b. Operating Performance

Evaluation of fluid-bed dryer performance is usually based on the stability of bed particle-size distribution. Results from runs made during this period are summarized in Figure 9, in which the particle-size distribution is plotted for the initial and final beds.

During the first two runs made with zirconium oxide bed material, considerable particle growth occurred as a result of agglomeration of smaller particles. The formation of lumps caused premature shut-down. After the initial coating of zirconium fluoride was applied to the particles, the tendency for agglomeration diminished, and it was possible to operate the fluid-bed dryer successfully for 8.5 hours during Run ZCP-42. Some particle growth still occurred, but it did not lead to any operational difficulties.

By lowering the feed flow rate from 90 ml/min in Run ZCP-43, it was possible to dry the zirconium fluoride solution on a fresh bed of refractory zirconium oxide without rapid particle growth or caking of the bed. The operation experience from these runs indicates that refractory zirconium oxide is a good starting bed material, and that caking of the bed at the outset of a run can be avoided, particularly if a reduced feed rate is employed during the initial period of operation.

The operation of the fluid-bed dryer proceeded without any difficulties during low temperature Run ZCP-44. Consequently, the proved operating temperature range now extends from 450 C to 240 C. There was only slight particle growth during the 8.3-hour run.

It was not possible to operate the fluid-bed dryer with a calcium fluoride starting bed for extended periods without caking the bed, even though a low feed rate was employed. The bed caked into large lumps three to five hours after start-up on three successive runs. Precoating the calcium fluoride seed particles with a thin layer of zirconium fluoride did not seem to alleviate the caking tendency. Since there was little particle growth during the first few hours of these runs, contrary to runs with a zirconium oxide bed, the cause of the lump formation is not known. The results substantiate previous experience in which satisfactory operation was achieved only after the calcium fluoride was heavily coated with dried product. Meanwhile, substantial quantities of material were provided for fluorination studies.

Future runs will use feed solutions more nearly simulating those that may be encountered in actual practice, such as those prepared by dissolution of three weight per cent uranium-Zircaloy-2 alloys.

c. Composition of Calcined Solids

The nature of the materials produced in the fluid-bed dryer has not yet been completely characterized. However, it was of interest to determine the amount and nature of volatile substances remaining in the dried solids, since these would be volatilized during subsequent process steps. A series of tests was made in which samples were heated in an inert atmosphere at 450 C. The evolved gases were collected and identified as mixtures of hydrogen fluoride and water. The data, summarized in Table 19, show that the relative amounts of water and hydrogen fluoride evolved are not constant, nor is the weight loss constant. The amount of hydrogen fluoride evolved ranged from 0.73 to 1.74 per cent and was directly proportional to the heating time. The quantity of water evolved showed no consistent pattern and ranged from 0.18 to 4.80 per cent.

Table 19

VOLATILE MATERIAL EVOLVED DURING HEATING OF
FLUID-BED DRIED ZIRCONIUM FLUORIDE

Material prepared in 6-inch fluid-bed dryer
Temperature of Ignition: 450 C

Run No.	Preparation		Time of Ignition (hr)	Total Loss in Weight (%)	Material Evolved	
	Feed F/Zr Ratio	Dryer Temp (C)			H ₂ O (%)	HF (%)
ZCP-42	4.5	300	1.00	1.65	0.92	0.73
ZCP-42	4.5	300	1.25	1.07	0.18	0.89
ZCP-42	4.5	300	1.50	1.57	0.63	0.94
ZCP-38	10.0	300	2.50	2.95	1.21	1.74
ZC-103 ^a	4.5	350	1.50	5.63	4.80	0.83

^aMaterial prepared in 3-inch fluid-bed dryer

In order to help characterize the products from the fluid-bed dryer, several fluid-bed product samples have been studied by X-ray diffraction.* The zirconium fluoride species present in each have been tentatively identified. Zirconium fluoride solution dried at 450 C (Run ZCP-39) produced a solid containing zirconyl fluoride and zirconium oxide. This material was made from a solution containing a fluoride to zirconium mole ratio of ten. Materials produced at 300 C from similar solutions seem to be anhydrous zirconium tetrafluoride of two polymorphic forms: the product from Run ZCP-31 is probably a low-temperature

*X-ray diffraction studies by D. S. Flikkema.

polymorph, while the product from Run ZCP-38, which was an extension of Run ZCP-31, is primarily the high-temperature polymorph. None of the samples showed any indication of a hydrate being present. Similar X-ray studies on solids produced from feed solutions having low fluoride to zirconium ratio (4.5/1) will be made.

Chemical analyses of the dried products (Table 20) tend to substantiate the conclusions reached from X-ray data. From feed solutions containing 10/1 ratio of fluoride to zirconium, the product obtained after fluid-bed drying at 300 C appears by analysis to be substantially anhydrous zirconium tetrafluoride; when the solution is dried at 450 C, the product is apparently zirconyl fluoride with some zirconium oxide. The product obtained at 300 C from solutions having a 4.5/1 fluoride to zirconium ratio appears from the analyses to be either zirconium tetrafluoride or a mixture of this with zirconyl fluoride. Exact identification is not possible because of the presence in the solid of some of the original zirconium oxide bed as well as a small amount of uranyl fluoride.

Table 20

ELEMENTAL ANALYSES OF
FLUID-BED DRYER PRODUCTS

<u>Run No.</u>	<u>Feed F/Zr Ratio</u>	<u>Bed Temp (C)</u>	<u>Analyses (%)</u>	
			<u>Zr</u>	<u>F</u>
ZCP-31	10	300	47	42.4
ZCP-38	10	300	47	41.8
ZCP-39	10	450	56	19.3
ZCP-42	4.5	300	51.8	31.4 ^a

Theoretical Compositions

	<u>Zr</u>	<u>F</u>
ZrF ₄	54.5	45.5
ZrOF ₂	62.8	26.2

^aAbout 16 per cent of the starting ZrO₂ bed and 7 per cent of UO₂F₂ is estimated to be included in this sample.

Haendler²⁰ found that zirconium fluoride monohydrate evolves both water and hydrogen fluoride upon heating. The conditions under which the heating was conducted are not mentioned.

²⁰Haendler, Helmut M., Progress Report, NYO-3162 (October 15, 1952).

Tananayev, et al²¹ state that the monohydrate splits off two moles of hydrogen fluoride when heated, one mole at 267 C, the other at 306 C. However, in the fluid-bed dryer the solid products are continuously in contact with the evolved gases, hydrogen fluoride and water vapor. Thus the products obtained are not necessarily the same as those produced in a simple heating operation as was done by these workers.

Several spray drying tests are being performed to produce material for X-ray diffraction studies which will not be contaminated by any bed material. This material is made by spraying the zirconium fluoride solution on the wall of the six-inch dryer. The results of these studies may help contribute to the identification of the fluid-bed products.

2. Recovery of Uranium from Uranium-Zirconium Mixtures by Fluorination in a Fluidized Bed
(G. J. Vogel, A. Rashinskas, L. Marek)

a. Pilot-Plant Studies

Dried uranium-zirconium mixtures were fluorinated in a 2.5-inch diameter fluidized-bed reactor (see ANL-5789) previously used for continuous fluorination of uranium tetrafluoride, but presently modified for batch operation. In a typical fluorination run the dried residue was loaded into the reactor and fluidized with nitrogen while being heated to the reaction temperature. The run was started by adding fluorine to the nitrogen to give a 15 per cent mixture and was continued for four hours. The residue was then sampled and analyzed for uranium and the procedure replicated for as many four-hour periods as desired.

Results show that uranium removal of about 99 per cent can be achieved with certain materials, depending on the temperature and duration of the fluorination treatment. Approximately 99 per cent removal was attained for material containing the equivalent of a 10 weight per cent uranium alloy by fluorinating for four hours at 600 C or 12 hours at 500 C (Figure 10, Runs 5 and 8). Uranium analyses were by an X-ray spectral method which is at its limit of sensitivity for these low uranium concentrations. More accurate determination of uranium removal will be made by a more sensitive neutron activation analysis.

A five weight per cent alloy equivalent material dried at 240 C (ZCP-44) and fluorinated at 500 C gave results comparable to the 10 weight per cent material dried at 300 C, about 98 per cent of the uranium removed after eight hours of fluorination (Figure 10, Runs 5 and 11). Since the dryer operated for approximately the same length of time in producing the 5 and 10 per cent materials, i.e., the coating thickness on

²¹Tananayev, I. V., Nikolayev, N. S., and Buslayev, I. A., "Investigation of the System $\text{HF}-\text{ZrF}_4-\text{H}_2\text{O}$ by the Isothermic Solubility Method (Isotherm 0.5°)" Zhurnal Neorganicheskoi Khimii, 1 274-281 (1956).

the base material was the same, the data on the amount of uranium removed suggest that neither the uranium concentration nor the temperature of drying in these ranges, 5 to 10 per cent and 240 to 300 C, respectively, greatly affects the rate of uranium removal by fluorination. Data from gram-quantity, fixed-bed fluorination tests tend to confirm the absence of any great effect due to uranium concentration differences in this range: fluorination of mixtures containing 6.7 and 8.8 per cent uranium for two hours at 600 C removed 98.5 and 97.5 per cent of the uranium, respectively (as determined from neutron activation analyses).

Comparatively poor uranium removal was encountered when material in which the uranium had been precipitated as the tetrafluoride (by increasing the fluoride ion concentration) prior to drying (see Figure 10, Run 13) was fluorinated. Removal was 50 to 61 per cent complete at the end of four and eight hours, respectively, compared to 88 and 98 per cent for the unprecipitated material. Microscopic examination of the precipitated product after drying and after fluorination showed that the material had undergone no obvious change in structure.

Variables in the fluorination step, such as inlet gas composition, velocity and bed temperature, will be studied in subsequent runs, along with the effects of changes in variables in the previous drying step.

b. Corrosion in the Fluidized-Bed Fluorinator (W. B. Seefeldt, L. Hays, R. Breyne)

The fluid-bed fluorinator has been used most recently for the fluorination of uranium-zirconium fluorides from the fluid-bed dryer. Corrosion coupons were inserted into the unit prior to Run 6B. These were supported on a 1/4-inch nickel tube at two different elevations, both thought to be within the bed.

Scaling of the Monel reactor has been observed after each fluorination run, with higher temperatures producing greater quantities of

FIGURE 11
VERTICAL CONTOUR OF NICKEL CORROSION
TUBE IN FLUID-BED FLUORINATOR

corrosion product. The scaling appeared to be most severe well into the vapor phase, where coupons had not been inserted - this would not normally be expected. This behavior appears similar to the high vapor-phase attacks being experienced in the volatility fused salt corrosion work (see Volatility section of this report, page 48).

To verify that metal losses were accompanying the severe scaling, the coupon support tube was removed after Run 14 for dimensional change and sub-surface corrosion evaluation. The dimensional change data are now available and the results graphically presented in Figure 11.

In all runs made while the support tube was in place, the fluidizing gas was 15 per cent fluorine in nitrogen. A total of eight four-hour runs were made, five

at a bed temperature of 500 C, the balance at 600 C. The material being fluorinated has not been fully characterized, but is likely to consist of combinations of UF_4 , UO_2F_2 , ZrF_4 , and $ZrOF_2$ with small amounts of residual water. Known uranium contents of initial charges varied from three to six per cent. The gas phase leaving the fluid bed would be expected to contain fluorine, nitrogen, uranium hexafluoride, oxygen, hydrogen fluoride, zirconium fluoride, and possibly impurities.

The dimensional changes were determined by taking micrometer readings of the diameter of the support tube after corrosion products had been removed. Removal was effected by soaking in water and rubbing lightly with steel wool.

The tube showed a very low attack in the area of the fluid bed, which is estimated to reach a maximum height of about 18 inches. The most severe metal loss occurred at elevations of 35 and 47 inches. The reason for this high attack is unclear at this time, but the explanation for two areas of high attack may be related to the two fluorination temperatures used.

A nickel support rod was placed in the unit following Run 14 in an effort to duplicate the above results.

3. Microscopic Examination of Fluid-Bed Products (J. Barghusen)

A microscopic examination of several fluid-bed dryer products was made to observe physical appearance of the particles after various treatments. The -20, +40 mesh fractions from several samples were mounted in Lucite and photographed. Considerable particle agglomeration occurred during the first of the series of runs made with zirconium oxide bed material, ZCP-40 (see Figure 12a). As the series progressed, Runs ZCP-41 and 42, agglomeration decreased and the particles became more spherical. The particles from the final bed from Run ZCP-42 show no agglomeration (Figure 12b). The uranium-containing shell, which seems to be more crystalline and less porous than the core, occupies about one-half the volume of the particle. Figure 12c shows the particles from Run ZCP-38. This sample was taken after a total running time of 75 hours, during which the calcium fluoride starting bed was essentially displaced.

Dried and fluorinated materials were compared to ascertain what happens to the physical structure of the particles during fluorination. The product from dryer Run ZCP-42 (Figure 12b) was fluorinated for 12 hours at both 500 C and 600 C (Runs U-Zr-6B and U-Zr-10, respectively). The fluorinated residues are shown in Figures 13a and 13b. The cores of these particles were apparently preferentially removed during fluorination at the higher temperatures. Since the particles originally contained a zirconium oxide core, the reaction of fluorine with the oxide might produce a temperature high enough to volatilize some of the zirconium tetrafluoride, which has vapor pressures of 0.2, 6 and 70 mm Hg at 600, 700, and 800 C, respectively. Another explanation for the hollow spheres might be core (oxide) decrepitation during fluorination.

Fluorination of material produced in Run ZCP-38 for eight hours at 500 C (Run U-Zr-14) resulted in very poor uranium removal. The fluorinated particles showed no obvious structural change (compare Figure 12c with 13c). The non-porous, crystalline structure of the particles evidently did not allow the fluorine to penetrate the particles and react with the uranium. Since uranium has been more readily fluorinated from thin shells than from thick ones, diffusion of the fluorine into the particles may be a factor limiting the uranium volatilization.

4. Laboratory Fluorination Studies (O. Sandus, N. Levitz)

Previous laboratory fluorinations of solids containing 2.0 per cent or more uranium showed about 94 per cent uranium removal for fluid-bed dried material and about 98 per cent removal* for laboratory drop-wise dried material in two hours fluorination. The latter tests used feeds containing equivalent of 5 to 25 weight per cent uranium-zirconium alloys.

*Determined by neutron activation analyses. Reported earlier as 96 per cent or better from X-ray intensity ratio analyses.

Figure 12

PHOTOMICROGRAPHS OF FLUID-BED DRYER PRODUCTS

Particle size: -20 + 40 mesh
Magnification: 20 X
Dryer Temperature: 300 C

(12a) Run ZCP-40, 5 hours operation, ZrO_2 starting bed (12b) Run ZCP-42, 16 hours operation, ZrO_2 starting bed (12c) Run ZCP-38, 75 hours operation, CaF_2 starting bed

Figure 13

PHOTOMICROGRAPHS OF FLUID-BED FLUORINATION PRODUCTS

Particle Size: -20, + 40 mesh

Magnification: 26 X

(13a) Run ZCP-42, fluorinated 12 hours at 500 C

(13b) Run ZCP-42, fluorinated 12 hours at 600 C

(13c) Run ZCP-38, fluorinated 8 hours at 500 C

Materials containing less than one per cent uranium showed 60 to 85 per cent removal in two hours. The fluorinations were all conducted at 600 C.

a. Effect of Carbon Additive

Previous data indicated that higher uranium concentrations enhanced uranium removal, probably by furnishing more reaction sites and producing a more porous material through which fluorine may readily diffuse. Additives such as carbon or sulfate, which volatilize during fluorination, were expected to produce a similar effect. A sample containing about 2.0 per cent uranium and 10 moles of carbon (added as dextrose) per mole of uranium was fluorinated for two hours at 600 C. Initially, 20 moles of carbon were added to the liquid feed per mole of uranium, but apparently about half of the carbon oxidized during the drying step. The results showed about 87 per cent removal of uranium and about 96 per cent removal of carbon. Thus no improvement in uranium removal as a result of carbon addition was obtained. Tests using other additives (such as sulfate) are planned.

b. Effect of Precipitation of Uranium Tetrafluoride during Fluid-Bed Drying

As described in the previous report (ANL-5896, page 59), the use of a uranium tetrafluoride slurry feed in the fluid-bed dryer did not improve uranium removal during fluorination. Some additional samples prepared by this technique were fluorinated in this quarter. A sample containing about 2.0 per cent uranium showed about 93 per cent removal, similar to that obtained for samples prepared from feed containing soluble uranyl fluoride. A previous fluorination on material containing 0.7 per cent precipitated uranium, which had been prepared in the fluid-bed dryer at 300 C, showed only 60 per cent removal. When the same solution was dried at 450 C, the uranium removal after fluorination was 89 per cent. Thus the higher drying temperature appeared to improve uranium removal in this case for reasons that are not yet understood.

c. Effect of Metal Additives

Since solids prepared by drying solutions in the laboratory in polythene equipment frequently showed greater uranium removal on fluorination than those prepared in the fluid-bed pilot plant, a study was made of the effect of metal impurities present as a result of corrosion of the pilot-plant Monel dissolver and the stainless steel feed tank. Presence of such impurities might inhibit volatilization of trace amounts of uranium. Copper, nickel and chromium salts were added to the uranium-zirconium fluoride solutions in concentrations equal to five times that of the uranium. Results of this series of fluorinations made at 600 C on materials containing 1.5 and 3.0 weight per cent equivalents showed little or no effect of the impurity additions. Pilot-plant fluid-bed fluorinations of fluid-bed dryer

products have further substantiated the negligible effect of metal contaminants, since about 99 per cent uranium removal has currently been achieved despite their presence.

B. Calcination of Reactor Fuel Processing Wastes

(E. L. Carls, J. W. Loeding, W. B. Seefeldt, C. Shoffstoll, R. Beck and W. D. Turner)

In the fluid-bed waste calcination process, liquid wastes resulting from spent fuel reprocessing are converted to solids in a heated fluidized bed. The solids are withdrawn to storage and the off-gases are treated for removal of entrained and volatile fission products. A number of methods for off-gas treatment are available, but the use of a venturi scrubber for particulate removal and a silica gel absorber for ruthenium removal is proposed for the plant-scale calciner to be installed at the ICPP. During this quarter the efficiency of a venturi scrubber and a silica gel absorber in removing volatile ruthenium from the calciner off-gas was examined in a series of runs using tracer ruthenium. The experimental equipment was described in the previous report (ANL-5896, page 66).

1. Ruthenium Decontamination Factors Across Venturi Scrubber and Silica Gel Adsorber

Table 21 shows over-all decontamination factors for ruthenium across the venturi scrubber and the silica gel adsorber. These were determined by cooling the gas leaving the adsorber to remove condensables and counting the radioactivity in the condensate. The presence of any non-condensable ruthenium was checked by passing the gas through filter paper. These decontamination factors are based on the assumption that 90 per cent of the feed ruthenium was volatilized. This assumption may be justified by examining the analysis of the solid product (Table 22), which indicates approximately 10 per cent of the feed ruthenium is retained by the alumina.

Previous experience had shown that ruthenium volatilization could be minimized by calcining at 500 C or higher. However, since the current runs were intended to study ruthenium removal from the gas, the calciner was operated at a temperature (400 C) known to produce high volatilization of ruthenium. Run HWC-49 was a tracer run in which only the silica gel adsorber was utilized, the venturi scrubber being by-passed. The temperature of the silica gel in the adsorber during this run rose to 135 C, which is considerably higher than the optimum temperature of 70 to 100 C based on laboratory studies performed by Phillips Petroleum Company at the ICPP. This probably accounts for the very poor ruthenium removal (less than a factor of 10) obtained in this run.

During the following tracer runs, both the adsorber and the scrubber were in the system. The temperature of the adsorber ranged from 80 C to 93 C for HWC-55 and from 68 C to 75 C for Runs HWC-57 and 58.

Table 21

RUTHENIUM DECONTAMINATION FACTORS ACROSS THE VENTURI
SCRUBBER AND SILICA GEL ADSORBER

Time After Start of Feed (hr)	Condensate, % of Feed Ru				Non-Condensables, % of Feed Ru				Ruthenium DF ^b			
	HWC-49 ^a	HWC-55	HWC-57	HWC-58	HWC-49 ^a	HWC-55	HWC-57	HWC-58	HWC-49 ^a	HWC-55	HWC-57	HWC-58
1	6.0×10^{-2}	1.7×10^{-1}	3.0×10^{-1}	5.0×10^{-2}	1.4×10^{-4}	1.1×10^{-4}	2.0×10^{-4}	1.9×10^{-4}	1500	520	300	1800
2	5.3	1.1×10^{-1}	2.8×10^{-1}	1.2×10^{-1}	-	-	-	-	17	820	320	250
3	16.8	5.0×10^{-2}	1.9×10^{-1}	1.3×10^{-1}	-	-	1.4×10^{-4}	6.0×10^{-5}	54	1800	470	600
4	25.0	26.0 ^c	1.3×10^{-1}	-	1.5×10^{-4}	8.0×10^{-4}	-	-	36	350 ^c	690	-
4.5	-	51.5 ^c	-	-	-	-	-	-	-	17 ^c	-	-
5	24.6	9.6	1.2×10^{-1}	1.6×10^{-1}	-	4.5×10^{-4}	-	-	36	94	700	560
6	-	2.7	-	1.9×10^{-1}	1.3×10^{-4}	-	-	1.0×10^{-4}	-	33	-	470

^aVenturi Scrubber bypassed^bBased on 90% of feed ruthenium being volatilized^cAdsorber and scrubber bypassed for repairs

Table 22

RUTHENIUM MATERIAL BALANCES

Temperature: 400 C

Feed Activity: 1×10^5 cpm/ml Ru¹⁰⁶-Rh¹⁰⁶ γ

Per Cent Feed Ruthenium in							Ruthenium Accounted For (%)
Run No.	Condensate	Non-Condensable Off-Gas	Product	Venturi Scrub Solution	Silica Gel Adsorber		
HWC-49	0.6 to 24.6	1.3×10^{-4} to 1.5×10^{-4}	12.0	-- ^b	40.0 ^c	52	
HWC-55	0.05 to 0.17 ^a	1.1×10^{-4} to 8.0×10^{-4}	10.3	14.9	40.0 ^c	65	
HWC-57	0.12 to 0.30	1.4×10^{-4} to 2.0×10^{-4}	8.2	20.6	40.0 ^c	69	
HWC-58	0.05 to 0.19	6.0×10^{-5} to 1.9×10^{-4}	5.5	19.4	21.6	47	

^aDuring time adsorber and scrubber were in system^bScrubber not in system.^cAveraged over the three runs.

The temperature of the gas leaving the venturi scrubber ranged from 61 to 63 C and was reheated about 10 degrees before entering the adsorber. The best decontamination factor achieved was 1.8×10^3 , while the majority of the decontamination factors ranged from 500 to 800. The percentage of feed ruthenium in the condensate ranged from 0.05 to 0.30. This compares with 40 per cent previously found in the condensate for similar runs prior to the installation of the venturi scrubber and silica gel adsorber. It should also be noted that during Run HWC-55, repairs necessitated bypassing the adsorber and the scrubber for approximately one hour, during which time the ruthenium content of the condensate rose to 52 per cent of the feed ruthenium.

Figure 14 is a plot of normality and activity of the venturi recycle scrub solution versus hours of usage for Run HWC-55 and Runs HWC-57 and 58. The same solution was used for Runs HWC-57 and 58. The steady-state acidity of the scrub solution was about five normal. The ruthenium content of the scrub solution increased linearly with time. The ruthenium removed by the scrubber amounted to 15 and 20 per cent of the feed ruthenium.

2. Silica Gel Adsorber Regeneration

The silica gel adsorber was backwashed several times to ascertain the amount of ruthenium activity held up. The first regeneration backwash was performed after Run HWC-55. The wash consisted of a volume of cold water equal to 0.75 times the bed volume of the silica gel. This procedure left some ruthenium on the silica gel. The second and third backwashes (Figure 15) consisted of 1.75 bed volumes of warm water. During the second backwash after Run HWC-57, 96 per cent of the removable ruthenium present on the silica gel was extracted. This was determined by graphical integration of the curve in Figure 15. These data, together with information from the first backwash, disclosed that for each run (HWC-49, HWC-55, HWC-57) an average of 40 per cent of the feed ruthenium was accounted for in the adsorber. The third regeneration was done

FIGURE 15
REGENERATION OF SILICA GEL ADSORBER

after Run HWC-58. Essentially 98 per cent of the removed ruthenium was extracted after 0.4 bed volumes of backwash had passed through the adsorber. The percentage of feed ruthenium found in the adsorber after Run HWC-58 was 21.6. It is not known with certainty that the regenerating wash water was distributed over the entire bed of silica gel in any of the regenerations. This will be checked in future regenerations by flooding the entire bed with water.

3. Material Balances for Tracer Runs

Table 22 shows the ruthenium material balance for the tracer runs. It may be noted that only 50 to 70 per cent of the ruthenium fed to the calciner was accounted for. In an attempt to locate the "missing" ruthenium, the off-gas pipework was surveyed with a β - γ radiation survey meter. Several "hot" locations were found in the piping, indicating that some ruthenium had probably plated out on cooler portions of valves and fittings. This is consistent with previous experience.

Efforts are being made to determine if the amount of ruthenium that plates out is increasing with each run, or if a steady state has been reached. This is being done by surveying portions of the pipework with a β - γ meter before and after runs.

Several spike runs involving dilution of ICPP waste have been made. One of these was an 80-hour extended run in which it is felt that a steady-state condition was reached. It is hoped that the results of these runs will reveal more significant data regarding such factors as the equilibrium level of activity in the condensate and the non-condensable off-gas, the equilibrium acidity of the venturi recycle scrub solution, decontamination factors across the venturi scrubber, and over-all decontamination factors for the equipment. More significant material balances for ruthenium may also be obtained.

4. Equipment Testing of Filters

a. Pressure-Drop Experiments

More complete data dealing with the relationship between pressure drop and filter area during filtration of gas-entrained fines from fluidized aluminum oxide have been obtained. Tests were conducted in the prototype of the proposed filter blowback system previously described (ANL-5858, page 45), using new sintered stainless steel bayonet filters (10-micron pore). The filters were first checked with air containing no alumina and yielded results comparable to the manufacturer's data (1.7 inches water at two cfm/sq ft filter area). At these low flow rates the venturi orifices produced no significant effect on pressure drop. The filters were next tested with an alumina bed and, while still clean, produced the results shown in Figure 16. This "clean filter" curve was necessarily taken over a short time interval. Points on the "coated filter" curve (Figure 16) were obtained after a minimum of 16 hours of continuous automatic operation following the completion of the "clean filter" curve. The curves are essentially parallel and are displaced about 12 inches water from one another. At two air rates, 12.8 and 15.8 cfm, the fluidizing air was momentarily halted and the filters blown back. The results indicate virtually complete cleaning of the filters by this mechanism.

b. Testing of New Equipment

As a proposed alternate to the sintered stainless steel filters, fiber glass filter elements were tested in the same equipment previously used in venturi blowback tests. After 18 days of testing, gram quantities of alumina were detected downstream from the filters. An inspection of the filters after shutdown revealed small holes in the cylindrical wall of the fiber glass element. As constituted, these filters appear to be unsatisfactory.

FIGURE 16
PRESSURE DROP ACROSS SINTERED METAL FILTERS WHILE IN OPERATION
WITH AUTOMATIC VENTURI BLOWBACK DEVICE

5. Corrosion Studies

(W. B. Seefeldt, L. Fuller,* R. Breyne)

The pilot-plant fluid-bed unit used for waste calcination studies utilizes an off-gas filter system consisting of sintered stainless steel bayonet-type filters. It may be recalled that some evidences of filter failure had been detected (ANL-5858, page 44) following carbon monoxide reduction runs. Several of these filters fractured, and others were weakened. A program has been undertaken to determine the cause and nature of this embrittlement so that corrective or preventive measures can be taken.

Calcinations made to date have been on Redox type wastes consisting mostly of aluminum nitrate, nitric acid, sodium nitrate, traces of mercuric nitrate, and fission product nitrates. These were conducted in a temperature range of 400 to 550 C, using nitrogen, air, and carbon monoxide as fluidizing gases. The latter, when used, was diluted with nitrogen. The bulk of the equipment was made of type 347 stainless steel, the sintered components of the bayonet filter of type 316 stainless steel. Temperature surges to 750 C were known to have occurred in runs involving carbon monoxide. These high temperatures may have contributed substantially to the corrosive effects ultimately resulting in filter fracture.

Several pieces of the sintered metal from the fractured filter were sectioned and examined metallographically. A piece from the fractured area showed substantial corrosion (Figure 17a); all edges exposed

*Summer employee from Cornell University.

Figure 17

REPRESENTATIVE CROSS SECTIONS OF FAILED SINTERED
STAINLESS STEEL FILTER FROM FLUID-BED CALCINER

Exposure

Environment: Nitrogen, air, or carbon monoxide
fluidizing gas containing calcination
products of Redox type wastes (aluminum
nitrate, nitric acid, sodium nitrate,
traces of mercuric and fission product
nitrates.)

Temperatures: 400 to 550 C with surges to 750 C when
using carbon monoxide.

Metal: Type 316 Stainless Steel

Magnification: 100X

(17a) Section from
embrittled area

(17b) Section from
apparently sound
area away from
fracture

to voids and to the gases contained corrosion deposits. A micrograph of a second area on the filter appears in Figure 17b. This area appeared to be reasonably sound mechanically, and the micrograph shows little of the corrosive attack seen in Figure 17a. By comparing the two, it becomes evident that the porosity in the latter has been reduced, suggesting that corrosion products have partially and completely filled the pores initially present.

Figure 18 shows a micrograph of a cross section of one of the solid stainless steel baffles that divided the bayonet filters into five groups of two each. A small amount of corrosion product is evident. Though it is not obvious from the micrographs, it is likely that the material is comparable to that formed in the pores of the filter. The magnification in Figure 18 is 400 X compared to 100 X in Figures 17a and 17b.

Figure 18

SECTION OF TYPE 347 STAINLESS STEEL FIN USED
TO DIVIDE FILTER ELEMENTS INTO GROUPS

Exposure

Environment and temperature: Same as in Figure 12

Magnification: 400 X

In order to learn more about this type of corrosion, experimental equipment was set up for small-scale laboratory runs. A schematic diagram of this equipment is shown in Figure 19. Nitrogen, air or carbon monoxide may be used as the inlet gas. Three molar nitric acid is introduced at a proper rate just ahead of the preheater. The latter vaporizes the acid and heats the resulting gas mixture to the temperature of test prior to introduction into the test section. Sufficient gas is bled off between the preheater and test unit to maintain a pressure differential of six to eight inches of water across the test section. A thermocouple immediately downstream of the test specimen monitors specimen temperature.

FIGURE 19
SCHEMATIC DIAGRAM OF CORROSION TEST UNIT
FOR SINTERED STAINLESS STEEL FILTERS

Runs made to date used nitrogen or air with nitric acid vapor at 400 and 500 C. Sintered, type 316, stainless steel was used as the test material. The results, which are tabulated in Table 23, are inconclusive. In Run WC-4, which utilized nitrogen at 550 C, general corrosion was observed. This is shown in Figure 20. The exposure was 72 hours. Two repeats, first with air and again with nitrogen (WC-5 and WC-6), yielded

Table 23

RESULTS OF CORROSION TESTS OF SINTERED STAINLESS STEEL
TYPE 316 EXPOSED TO SIMULATED OFF-GASES
OF WASTE CALCINATION PROCESS

1. 2 ml/min of 3 M HNO_3 (liq) vaporized into gas stream
2. Pressure differential of 6 to 8 inches of water maintained across test section
3. All test sections degreased with acetone and ethyl alcohol
4. All gas rates are 6.75 liters per minute at one atmosphere, room temperature

Run Designation	Temp (C)	Time (hr)	Gas	Metallographic Observation
WC-1	400	7	N ₂	No corrosion observed
WC-2	400	4-3/4	N ₂	No corrosion observed
WC-3	550	24	N ₂	No corrosion observed
WC-4	550	72	N ₂	General corrosion through entire specimen visible at 100 X
WC-5	550	72	air	No corrosion observed at 100 X, some at 400 X
WC-6	550	72	N ₂	Same as WC-5
WC-7	550	96	air	No corrosion observed

Figure 20

TYPE 316 SINTERED STAINLESS STEEL AFTER EXPOSURE
TO SIMULATED WASTE CALCINER OFF-GASES

Exposure

Environment: Nitrogen containing vaporized 3 molar
nitric acid.

Temperature: 550 C

Time: 72 hrs

Magnification: 100X

Magnification: 400 X

only small amounts of corrosion, which was observable only at higher magnifications (400 X). A second repeat with air resulted in no observable corrosion. It is evident that some experimental parameter is not completely under control. No clear reason can be stated as to why the specimen from WC-4 showed serious attack and those from WC-5 through WC-7 did not. Further repetition is indicated.

When the above question is clarified, it is planned to introduce carbon monoxide into the apparatus.

6. Calcination of Synthetic Darex-Type Waste

A synthetic stainless steel feed approximating Darex waste was prepared and calcined in the fluid-bed unit as a feasibility study. The solution contained 50 g/l of dissolved metals as nitrates, approximately 74 per cent iron, 18 per cent chromium, and 8 per cent nickel. The starting bed was alumina which was maintained at 400 C. The feed rate was ca 95 ml/min and run time was 8.5 hours. Operations were satisfactory. The product, however, contained an unusually large number of fines, as compared to previous experience with alumina product, and proved to be considerably softer. The calcined oxides could quite easily be removed from the alumina core by rubbing between the fingers. Dusting and transportation might prove to be troublesome factors in handling the product; excessive fines production might hamper fluidization. Different operating conditions might result in a more favorable product.

C. Mixing Studies in Straight and Tapered Fluidized Beds (H. Littman)

Preliminary experiments have been completed in a study of solids mixing in straight and tapered fluidized beds. The procedure and equipment used are described in ANL-5858, pages 51 to 53. Runs were made with copper spheres of minus 140, plus 200 mesh and minus 20, plus 40 mesh sizes, using dry air at room temperature as the fluidizing medium.

The mixing of the minus 140 plus 200 mesh particles in a straight column follows the diffusion equation reasonably well. A mixing coefficient of 0.005 sq ft/sec, independent of gas velocity, was obtained. For the tapered bed mixing did not follow the diffusion equation and was retarded, although the rate of mixing did increase with increasing flow rate. Also, slugging and bed expansion were reduced in the tapered bed. All of these effects were accentuated for the minus 20, plus 40 mesh particles in the tapered bed. Deep beds of coarse particles in straight columns were found to operate poorly because of excessive slugging.

The minimum fluidizing velocity is slightly higher in a tapered than in an untapered bed. The pressure drop at fluidization in the tapered bed

can be calculated from the ordinary pressure drop equation, i.e., by dividing the bed weight by the arithmetic average cross-sectional area. This means that the tapered bed handles a greater bed weight per unit of pressure drop than an untapered one, which may be an advantage in certain process considerations.

Future work in straight columns will be concerned with the effect of bed height on the mixing coefficient. In tapered beds more runs will be made investigating the effects of bed height, gas velocity and counter location. A theory will be sought to describe the mixing in the tapered bed. A preliminary topical report is in preparation.

D. Study of the Factors Influencing Particle Growth in a Fluid-Bed Calciner (B. S. Lee)

Calcination in a fluidized bed involves the continuous spraying of a liquid feed into a column of heated fluidized solids. The bed is made up of calcined product particles. This process was conceived to utilize the good heat transfer characteristics and uniform temperature distribution inherent in a fluidized bed. The unit developed at Argonne (ANL-5290, pages 111 to 118) for the calcination of uranyl nitrate operated satisfactorily under conditions where particle growth in the bed was controlled. Since the stability of a fluidized bed is intimately associated with the bed particle size, the factors that influence particle growth must be determined before successful operating conditions can be predicted. However, these factors are numerous and interrelated so that at present a trial-and-error technique is used to arrive at conditions that will give satisfactory performance. This project was initiated to study some of these factors and it is hoped the data can be correlated so that the prediction of proper operating conditions may be feasible.

The fluidized-bed calciner combines the features of both spray drying and fluidization. Therefore, factors affecting both these unit operations should be considered in this study. A literature survey was made, and, although considerable work had been done on spray drying and fluidization separately, little information was available on their combined effects.

In a calciner the average particle size increases by two mechanisms: agglomeration of small particles and the normal growth due to continuous spraying, while a decrease in size may be due to attrition and formation of excess nuclei. Since it is extremely difficult to study all the mechanisms simultaneously, it is proposed that they be studied individually at first and later cumulatively.

In previous runs made with uranyl nitrate, there was a considerable tendency for small particles to agglomerate and form large particles. This may be due to the fact that uranyl nitrate goes through a doughy stage during dehydration and denitration. To eliminate agglomeration in the first phase

of this study, a material of high melting point (851 C), sodium carbonate, was chosen. Sodium carbonate, unlike uranyl nitrate which decomposes at temperatures below 300 C, is stable chemically in the 300 C range. Thus drying can be studied independently of chemical reaction.

Microscopic examination of dried particles of various materials from previous runs in the six-inch pilot plant column showed a concentric ring-like structure. If the thickness of successive growth rings could be measured reliably, it would be possible to estimate the residence time in the spray zone, the amount of feed picked up, and the circulation rate in the bed.

A three-inch column, previously used for calcination of aluminum nitrate solutions, was used for the preliminary calciner tests. The starting bed was a minus 40, plus 60 sieve fraction of sodium carbonate particles. The column was operated at 300 C, atmospheric pressure, with air as the fluidizing medium. A 0.030-inch feed nozzle with atomizing air pressure of 20 to 25 psig was used. Two successful runs of four and seven hours were made with 10 per cent sodium carbonate solution at 20 ml/min. Nozzle plugging occurred in some runs, so a cooling coil was wrapped around the nozzle to reduce pre-vaporization of the feed in the nozzle before entering the bed. The products from these runs contained fractions of plus 40 as well as minus 60 mesh particles. To determine how much of the minus 60 fraction was due to attrition, an attrition run lasting six hours was made. The attrition run was carried out under the same operating conditions as the other runs, except no feed was introduced. About 29 per cent of the starting bed of 40 to 60 mesh particles was decreased in size to the minus 60 range. Further attrition runs will be made so that the contribution of the nozzle atomizing air to the formation of fine particles can be ascertained.

The products produced in the sodium carbonate drying runs were mounted in Lucite, sectioned, and polished. Microscopic examination showed uniform particles with no visible ring structure. Color-dyed feed will be alternated with the plain feed in the next series of runs in the hope of obtaining visible growth rings of different colors.

IV. REACTOR CHEMISTRY

The study of factors influencing pyrophoricity and oxidation of the reactor materials, uranium, zirconium, thorium, and plutonium has continued to progress.

In the uranium burning-curve test, variation of the oxygen flow rate has shown a negligible effect. However, decrease of the heating rate causes a decrease of the ignition temperature, indicating that burning-curve ignition test results should only be used for the comparisons of other variables.

The specific area dependence appears to dominate the additive influence since the effects of additives of aluminum and copper on the ignition temperature of 8.5-mm uranium cubes in oxygen were not shown for 0.25-mm foils. In an effort to understand the thermocycling phenomena observed when uranium reacts with air, studies in helium-oxygen and nitrogen-oxygen mixtures have been undertaken. Startling differences have been shown between the reactions in the two systems and between the reactions of two sources of pure uranium. Continued studies include the use of very high-temperature thermocouples to measure the maximum burning temperature of the metal.

The microscopic observation of the surface during isothermal oxidation of uranium suggests two simultaneous processes are involved.

An ignition test has been developed in which zirconium foil specimens were electrically heated to a high temperature in very short times. The ignition, current, and voltage were simultaneously recorded by means of oscilloscopes and a Fastax camera. Preliminary tests have shown marked differences between the behavior of both zirconium and a titanium-zirconium alloy in both oxygen and air. Zirconium shielded ignition tests using vacuum for prevention of oxidation during heating, or using annealing to produce an unoxidized surface (by dissolving oxide into the zirconium), have not produced lower ignition temperatures than helium shielded tests.

The oxidations of 60 binary zirconium alloys have been completed. The effects of each of the 20 additives in concentrations of 1, 2, and 4 atom per cent have been compared in terms of breakaway phenomena, cubic and parabolic rate constants, and total weight gain. Only copper, nickel, beryllium, and hafnium alloys showed increased oxidation resistance as compared to pure zirconium. The largest group of alloys, including pure zirconium, followed the cubic rate law for the entire extent of reaction up to 1400 minutes. The second largest group showed breakaway phenomena after initially following the cubic rate law. Some of the alloys followed the parabolic rate law with subsequent breakaway.

A short-term study of magnesium ignition has shown disagreements with results obtained by earlier experimenters. Shielded ignition tests were used to obtain an indication of an activation energy which suggests a magnesium vaporization process.

The experimental program to determine rates of reaction of molten reactor fuel and cladding metals with water is continuing. The principal laboratory-scale method involves the rapid melting and dispersion of metal wires in a water or steam environment by a surge current from a bank of condensers. The proposed method was presented in detail in the previous quarterly report, ANL-5896, page 101. Preliminary experience with the completed condenser discharge is reviewed. Equipment for use in the in-pile (TREAT) tests has been designed and is under construction.

A program has been undertaken with the Reactor Engineering Division to determine the feasibility of decontaminating the auxiliaries of a boiling water reactor following a fuel rupture. Coupons have been inserted into several locations in the EBWR for identification of activities and for decontamination studies. Laboratory autoclaves are now in use, and a pilot-plant loop that simulates reactor operation is being constructed and installed in a shielded cell.

The relative values of the neutron capture cross section of U^{238} for monoenergetic neutrons in the energy range 0.36 to 1.50 Mev have been determined. These values were normalized to the value in BNL-325, $\sigma = 0.130$ b at 0.360 Mev. The purpose of this work was to determine whether the small peak in the curve in BNL-325 in the region around 1 Mev is a real effect. The existence of the peak was corroborated.

Mr. H. Hembree, Reactor Development Branch, AEC, Washington, visited ANL September 9 to discuss metal oxidation-ignition problems and metal-water reaction studies.

A. Metal Oxidation-Ignition Kinetics

(J. G. Schnizlein, H. A. Porte, P. J. Pizzolato, J. D. Bingle, D. F. Fischer, L. W. Mishler, P. Martin and R. C. Vogel)

1. Uranium Ignition Studies

a. Burning Curves - Oxygen Flow Rate Dependence

In most of the uranium burning-curve tests in oxygen, a flow rate of 1200 cc per min (500 cm per min linear velocity) has been used (see ANL-5759, page 79, ANL-5789, page 56, and ANL-5820, pages 67 to 76 for details of apparatus and procedure). Because the gas flow rate might be expected to influence the rate of heat loss from the sample, burning-curve tests were run with varied flow rates.

A vacuum-tight ignition apparatus was built of quartz so that static oxygen burning curves could be run. Three burning curves for Argonne-base uranium in O (static), 1200 and 2600 cc per min oxygen flow rates are compared in Figure 21. The change of shape of the burning curve with varied flow rate was only slight. Identical ignition temperatures of

595 C were determined graphically from all three curves. The general slope of the burning curves increased slightly with decreased flow rate. The burning curve in the static oxygen atmosphere showed a slightly increased hump just above 400 C. These effects were probably due to the slightly lower heat losses from the sample to the gas stream at lower flow rates.

FIGURE 21
BURNING CURVES FOR ANL-BASE URANIUM IN OXYGEN

b. Burning Curves - Heating Rate Dependence

All burning-curve ignition tests of uranium and uranium alloys have been performed with a furnace temperature increase rate of 10 degrees per minute. A few tests with varied heating rates have shown that a decrease of the ignition temperature of pure uranium can be achieved by much slower heating rates.

Heating Rate (degrees/min)	Uranium	
	Ignition Temperature ANL Base	BMI Base
15	-	635
10	595	575
6.67	-	535
5	555	-
2.5	555	-

This further emphasized the empirical nature of ignition temperatures obtained by this method. Moreover, ignition phenomena are very strongly dependent on the balance of the heat of reaction and the heat losses due to the system used. For the purposes of studying other important variables, such as alloy or impurity content and specific area, the use of a standardized test procedure provided adequate comparisons of the effects. The reproducibility of the results attested to this hypothesis.

c. Specific Area Dependence of Alloys

Burning-curve tests for 8.5-mm cubes of uranium alloys in oxygen have shown (see ANL-5820, pages 67 to 76) that one atom per cent aluminum additive decreased the ignition temperature 200 degrees and that one atom per cent copper increased the ignition temperature approximately 200 degrees. It was important to determine if the effects of these additives applied to smaller particles, i.e., higher specific area.

Burning-curve tests of 3.5-mm cubes and 0.25-mm (10-mil) foils of these alloys were run in oxygen and ignition temperatures determined graphically. The 0.25-mm foils of aluminum and copper alloys showed the same ignition temperature (385 C) as Battelle-base uranium. The ignition temperatures for 8.5 and 3.5-mm cubes and 0.25-mm foils are compared in Table 24. The effect of the additives does not appear to apply to smaller particles, provided the rolling to foils has not produced a new effect. It was impossible to roll the alloys to thinner foils so that a greater extension of the specific area effect could be studied.

Table 24

COMPARISON OF EFFECTS OF SPECIFIC AREA AND ALUMINUM AND
COPPER ADDITIVES ON IGNITION TEMPERATURES IN OXYGEN

Sample Size	Approx. Specific Area (sq cm/g)	Ignition Temperature (C)		
		1 a/o Al	1 a/o Cu	B Base
8.5-mm cube	0.4	355	770	575
3.5-mm cube	1.0	360	540	540
0.25-mm foil	4.7	385	385	385

d. Burning Curves in Helium-Oxygen Mixtures

In order to separate some of the variables in comparing burning-curve ignition tests in oxygen with those run in air, mixtures of nitrogen and oxygen and of helium and oxygen were used as the oxidizing atmosphere. An increase of ignition temperature was observed when the oxygen is diluted with adequate helium. For Battelle-base uranium the ignition temperature was increased when the oxygen content of the atmosphere was reduced to 66 per cent. However, for Argonne-base uranium the ignition temperature was not increased until the oxygen was diluted to approximately 40 per cent. Further decrease of the oxygen content caused an increase of ignition temperature of approximately 15 degrees for each per cent concentration. The oxygen flow rate was maintained at 1200 cc per min and the helium flow rate varied to produce the selected composition. The dependence of ignition temperature on oxygen content in helium is shown in Figure 22 for both Argonne-base and Battelle-base uranium. In equivalent oxygen contents the Argonne-base uranium had a lower ignition temperature than the Battelle-base. The difference in behavior of these two sources of pure uranium is remarkable, considering the minor differences of impurity content (see Table 25). The only obvious difference was in the metallurgical history, i.e., Argonne base has been β -quenched while Battelle base was in its as-cast structure.

FIGURE 22
URANIUM IGNITION TEMPERATURES
IN HELIUM-OXYGEN MIXTURES

Table 25

IMPURITY CONTENT OF URANIUM

(Parts per million)

Impurity Elements	Argonne Base ^a (β -quenched)	Battelle Base ^b (as-cast)	Impurity Elements	Argonne Base ^a (β -quenched)	Battelle Base ^b (as-cast)
O	12	19	Ni	15	30
C	21	69	Al	15	34
H	5	0.5	Cr	5	30
N	56	22	Mn	2	4
Si	30 to 50	20	Mg	3	2
Fe	45	50	Cu	2 to 5	3

^aThe Argonne-base uranium was used for base-line data (β -quenched).

^bThe Battelle-base uranium was used for fabrication of the alloys (as-cast).

e. Reaction with Air at High Temperature

Burning-curve tests of uranium in air have neither shown the same characteristic bright flash upon ignition observed in oxygen nor was the burning sustained. Samples in air self-heated as high as 1500 C, but within about two minutes the temperature decreased to approximately 800 C, followed by a continued thermocycling periodic process until the samples were consumed. Burning curves for Argonne-base uranium in oxygen and in an 80 per cent nitrogen - 20 per cent oxygen mixture are compared in Figure 23. Additional studies were made in various oxygen-nitrogen mixtures. The ignition temperature was determined in the usual graphic manner, ignoring the subsequent cooling and thermocycling where they occurred. When the oxygen content was diluted to 60 per cent with nitrogen, no increase of ignition temperature was observed. In 50 per cent oxygen the ignition temperature increased markedly, but continued dilution of the oxygen with nitrogen caused the ignition temperature to decrease and the thermocyclic process to become more obvious, as shown for the 20-80 oxygen-nitrogen mixture. These ignition temperatures are compared in Figure 24 with those obtained in helium-oxygen mixtures with similar oxygen contents.

For continuing studies a very high-temperature thermo-couple (rhenium-tungsten) is being used to observe the burning temperature and to learn more of the delicate balance between heat of reaction and heat loss needed to sustain burning in air.

FIGURE 23
BURNING CURVES FOR ANL-BASE URANIUM IN OXYGEN AND
20 PER CENT OXYGEN - 80 PER CENT NITROGEN MIXTURE
(1200 cc/min OXYGEN IN EACH)

FIGURE 24
IGNITION TEMPERATURES OF ANL-BASE URANIUM IN
HELIUM-OXYGEN AND NITROGEN-OXYGEN MIXTURES

2. Uranium Isothermal Oxidation

a. Microscopic Observation

The study of surface changes in an oxidizing specimen of uranium by means of the microscopic hot-stage technique has been continued. Some understanding of the reaction mechanism may be gained from a correlation of physical changes in the oxide surface with the kinetics of the reaction. Using the vacuum induction heating stage previously described (see ANL-5896, page 84), it has been possible to follow visually the progress of the oxidation of a uranium specimen while the oxygen consumption was measured by means of the volumetric apparatus. Although results varied somewhat in specimens oxidized under what would appear to be the same conditions, in each case the course of events followed a similar pattern. While the uranium sample was being heated to the desired operating temperature, 200 C, the metal surface quickly became covered with a thin film of oxide, even though the sample chamber was being evacuated. The sample darkened in color and the initial sharp contrast between grains diminished very rapidly. These changes tend to suggest that in the initial states, at least, the whole surface was being covered by an oxide film of relatively uniform thickness. When the sample was at the appropriate temperature, oxygen was admitted. During the continuing formation of the smooth oxide film, small nuclei or nodules of oxide formed on the film and gradually spread over the surface by lateral growth. The progress of the growth of oxide in a typical case is shown in a series of micrographs (Figure 25 a to f) taken at various times during the course of the oxidation. Figure 25b shows small nuclei or nodules growing on the surface after five minutes of oxidation. As the oxidation proceeded, there was accelerated growth of nodules, as well as nucleation of additional nodules. Some of the nodules appear and grow rapidly, while others grow only very slowly or become dormant after a period of rapid growth. Nodules which were close together tended to coalesce during the process of growth. In some cases there appeared to be a correlation of the nucleation of nodules with surface irregularities. In the sequence of micrographs shown in Figure 25, for example, nodules showing the fastest growth rates were characterized by dark patches located at their centers. Since these dark patches did not appear to change in size very much during oxidation, it is possible that they were inclusions in the metal surface which acted as nucleation sites.

There appears to be no obvious correlation between either the onset of nucleation or the complete coverage by oxide nodules and the transition from a slow linear rate to a fast rate known to occur in the reaction kinetics (see ANL-5602, pages 65 to 86, ANL-5668, pages 52 to 60, and ANL-5630, pages 60 to 68). In each case the first nucleation of nodules was observed very early in the oxidation and the surface was not completely covered by the growing oxide nodules until well after the transition took place.

(a) As polished - 1μ finish

(b) 5 min.

(c) 10 min.

Fig. 25 a, b, and c. Micrographs of Surface Oxidation of Uranium at 200 °C in 200 mm Oxygen for Designated Times.

(d) 20 min.; $15\mu\text{g}$ oxygen consumed per sq cm

(e) 45 min.; $134\mu\text{g}$ oxygen per sq cm

(f) 85 min.; $418\mu\text{g}$ oxygen per sq cm

Fig. 25 d, e, and f. Micrographs of Surface Oxidation of Uranium at 200 C in 200 mm Oxygen for Designated Times.

3. Zirconium Ignition Studies

a. Electrical Heating Test

To date, two procedures for studying ignition characteristics have been developed. Burning-curve and shielded tests have been applied to uranium. The shielded tests have been applied to zirconium. Development of experimental methods for studying ignition characteristics is an essential part of the program.

An ignition test has been developed in which zirconium foil specimens ($0.32 \times 1.27 \times 0.014$ cm) could be electrically heated to a high temperature in very short times. The essential features of the system are shown in Figure 26. The data were recorded by the Fastax camera which can simultaneously record (1) the ignition, (2) current, and (3) voltage. Brass electrodes, 1.1 cm apart, gave good electrical contact with the specimens. The use of a mirror allowed both current and voltage to be photographed through one of the Fastax camera windows. The ignition was photographed through the other window. The current which passed through the sample in a period of time, i.e., the heating rate, was changed by the variac in the circuit.

FIGURE 26
ZIRCONIUM ELECTRICAL HEATING APPARATUS

The experiments were started by the Fastax camera controller which started the camera and after a short time interval started the electrical heating. The electrical heating was continued until sample failure occurred. Voltage and current were traced on the oscilloscopes. When the sample ignited or broke, the current fell to zero. The entire experiment took place in less than one second. Time-marking points along the edge of the film allowed one to calculate film speed, and, therefore, the chronology of the event, current, and voltage. Thus, the data

which could be obtained directly from the film were time to sample glow, time to sample failure, voltage, and current. From these data the energy to glow, energy to failure, and the heating rate were calculated.

Preliminary ignition tests have been run on pure zirconium and the 1.1 atom per cent titanium alloy foils in both oxygen and air. The data are summarized in Table 26. In oxygen the samples ignited violently and were completely consumed. In air the samples glowed brightly until they broke.

Table 26

ELECTRICAL HEATING OF ZIRCONIUM AND ZIRCONIUM-1.08 ATOM PER CENT
TITANIUM ALLOY FOILS

Foil (5-mil)	Gas	Time to Sample Glow (msec)	Time to Sample Failure (msec)	E (volts)	I (amp)	Energy to Glow (cal)	Energy to Failure (cal)	Heating Rate (cal/msec $\times 10^2$)
Zr	Oxygen	136	174	3.79	48.1	5.9	7.5	4.32
Zr	Oxygen	272	333	2.74	36.6	6.5	8.0	2.39
Zr	Oxygen	496	612	2.00	26.0	6.2	7.6	1.25
Zr - 1.08 at % Ti	Oxygen	92	127	3.90	52.4	4.4	6.1	4.81
Zr	Air	78	337	3.81	51.2	3.6	15.7	4.66
Zr - 1.08 at % Ti	Air	104	300	3.97	48.3	4.8	13.8	4.59

Pure zirconium foil was tested in oxygen at three different heating rates. Although the variation of the heating rate was slightly more than a factor of three, no obvious change of the energies to sample glow and failure implies that the heat loss was equal for the different heating rates. In oxygen the 1.1 atom per cent titanium foil glowed and failed at shorter times and required less energy to glow and fail than did pure zirconium. In air both the pure zirconium and the titanium alloy took longer to fail than, and required about twice as much energy as, the corresponding run in oxygen. The pure zirconium required a longer time, and more energy to fail, than the 1.1 atom per cent titanium alloy. However, the time and energy necessary for glow were less for pure zirconium than for the 1.1 atom per cent titanium alloy.

Some qualitative agreement can be seen between the results obtained in these tests with results obtained on the shielded ignition apparatus (see ANL-5896, pages 93 to 98) in oxygen and in air. With the shielded ignition apparatus, the ignition temperatures of zirconium foils were higher than the 1.1 atom per cent titanium foils in both oxygen and in air; in the electrical apparatus, the energies to failure of zirconium foils were 1.4 and 1.9 calories higher than the 1.1 atom per cent titanium foils in oxygen and air, respectively.

However, a point of contradiction exists between results obtained by the two ignition tests. In the shielded ignition tests the ignition temperatures of zirconium in oxygen were identical with the ignition temperature in air. The 1.1 atom per cent titanium alloy also showed the same ignition temperature in air as in oxygen. However, in the electrical heating test the energy to failure of zirconium in oxygen was about half as much as the energy required in air. The same results were obtained for the titanium alloy. The reason for this apparent discrepancy is not understood, but it further emphasizes the qualitative observations (see ANL-5896, pages 93 to 98) for shielded ignition tests comparing air and oxygen, i.e., prolonged glow, lack of complete consumption and modest temperature increase instead of bright flash, complete consumption of sample, and temperature increase to greater than 1400 C.

After making these preliminary runs it was felt that more information could be obtained from this type of test if the electrical heating could be stopped before the sample failed. Therefore, the apparatus is being modified to include a time switch which will control the length of time that the specimen is heated. With this change in the apparatus it should be possible to heat a specimen to some temperature (short of failure) and then observe whether or not the specimen can self-heat to ignition.

b. Ignition Tests in Isothermal Apparatus

Ignition tests in oxygen have been run on five-mil zirconium foil in the isothermal apparatus. The purpose of these experiments was to see whether lower ignition temperatures than 796 C [obtained (see ANL-5896, pages 93 to 98) in the shielded ignition apparatus] could be obtained if the specimens were heated to temperature in 10^{-6} mm vacuum. The hypothesis was that the surface of the specimens would be less contaminated if heated in vacuum than they were in shielded tests heated in flowing helium. The lowest ignition temperature that could be obtained in 760 mm oxygen after heating to test temperature in vacuum was 815 C.

In a further attempt to obtain a clean unoxidized surface, samples were heated to 900 C for three hours in vacuum (10^{-6} mm) to allow surface oxide to dissolve into the metal, and then cooled to the test temperature before oxygen was admitted. The lowest temperature at which ignition was observed was 825 C. It is felt that the reason higher ignition temperatures were obtained was due to the extreme "gettering" capability of zirconium and inadequate vacuum to remove sufficiently adsorbed gases from the glass walls. Perhaps a lower ignition temperature could be obtained in a system capable of vacuums of 10^{-10} or 10^{-11} mm.

c. Zirconium Shielded Ignition Tests

Five-mil foils of the following zirconium-base alloys have been fabricated: one atom per cent nickel, four atom per cent aluminum, two atom per cent titanium, and two atom per cent uranium. Shielded ignition tests on these alloys in oxygen and in air are now in progress.

4. Zirconium Alloy Isothermal Oxidation

The oxidation of a series of zirconium-base binary alloys at 700 C and 200 mm of mercury of oxygen has been completed. Alloys of aluminum, beryllium, carbon, chromium, cobalt, copper, hafnium, iron, lead, molybdenum, nickel, niobium, platinum, silicon, tantalum, tin, titanium, tungsten, uranium, and vanadium with crystal bar zirconium (see ANL-5789, page 75) were studied. Each binary system included three nominal compositions: one, two, and four atom per cent, except that the four atom per cent tungsten alloy was impossible to fabricate. In most cases, duplicate oxidation runs were performed and averaged.

A correlation of the weight gain in the first minute with the ignition temperatures has been demonstrated (see ANL-5896, pages 93 to 98). The general oxidation characteristics of the alloys are illustrated in Figure 27 where four different modes of reactor behavior are represented. The initial rate, breakaway, and total weight gain data are presented in Tables 27 and 28.

The largest group of alloys, including pure zirconium (Table 27 and bottom bracket Figure 27), showed no breakaway phenomena and oxidized as long as 1400 minutes according to the cubic rate law, i.e., the slopes of log weight gain versus log time plots were in the range 0.29 to 0.40. The cubic rate constants ranged from 0.78×10^7 to $496 \times 10^7 \mu\text{g}^3\text{cm}^{-6}\text{min}^{-1}$.

The one and two atom per cent tantalum alloys showed no breakaway phenomena up to 500 minutes and oxidized according to the parabolic rate law, i.e., had log-log slopes of 0.60 and 0.66. The parabolic rate constants were 39.5×10^4 and $30.5 \times 10^4 \mu\text{g}^2\text{cm}^{-4}\text{min}^{-1}$, respectively.

Another large group of alloys showed breakaway phenomena after oxidizing initially according to the cubic rate law, $1/n = 0.28$ to 0.39 . The cubic rate constants ranged from 0.49×10^7 to $251 \times 10^7 \mu\text{g}^3\text{cm}^{-6}\text{min}^{-1}$. Breakaway times ranged from 6 to 655 minutes, and breakaway weights ranged from 439 to 9468 $\mu\text{g}/\text{sq cm}$. After the breakaways, faster linear rates, ranging from 1.7 to 292 $\mu\text{g cm}^{-2}\text{min}^{-1}$, were followed for the duration of the run.

FIGURE 27
OXIDATION OF VARIOUS ZIRCONIUM-BASE ALLOYS
AT 700 C AND 200 mm OXYGEN
GENERAL OXIDATION CHARACTERISTICS

The last group of alloys (top bracket Figure 27) showed break-away phenomena after initial parabolic oxidations. The parabolic rate constants range from 2.2×10^4 to $106 \times 10^4 \mu\text{g}^2\text{cm}^{-4}\text{min}^{-1}$. Breakaway times ranged from 23 to 500 minutes, and breakaway weights varied from 1076 to 14,450 $\mu\text{g}/\text{sq cm}$. The faster linear rates after breakaways ranged from 7.7 to 30.2 $\mu\text{g cm}^{-2}\text{min}^{-1}$.

The breakaway evidently takes place when the oxide film loses its protective character. The breakdown of the protective oxide film does not appear to be related to any particular weight gain, since breakaway weights ranging from 439 to 14,450 $\mu\text{g}/\text{sq cm}$ have been observed. However, the color and character of the oxide films of alloys that had undergone breakaways (see Table 28) were definitely different from the protective oxide films that were on other alloys (see Table 27). For alloys where no breakaways occurred the oxide films were usually gray or black and very adherent. In contrast, on alloys where breakaways had occurred the oxide films were usually white or tan and readily flaked off.

Table 27

OXIDATION OF ZIRCONIUM-BASE ALLOYS WHICH FOLLOW THE
CUBIC RATE LAW WITH NO BREAKAWAY
 (700 C and 200 mm Oxygen)

Alloy Composition, Atom Per Cent (Balance Zr)	Slope of Log-Log Plot (1/n)	Cubic Rate Constant ($\mu\text{g}^3\text{cm}^{-6}\text{min}^{-1} \times 10^{-7}$)	Length of Run (min)	Weight Gain ($\mu\text{g}/\text{sq cm}$)	Color and Character of Oxide Film
Pure Zr	0.33	1.6	1400	2845	Blue-gray; adherent
1.08 Cu	0.34	1.1	1400	2458	Black; adherent
1.84 Cu	0.34	0.90	1400	2347	Black; adherent
3.60 Cu	0.33	0.78	1400	2385	Black; adherent
0.91 Ni	0.35	1.5	1400	2715	Black; adherent
2.48 Ni	0.34	1.1	1400	2484	Black; adherent
4.22 Ni	0.32	1.0	1400	2436	Gray-gold tinge; adherent
0.90 Be	0.29	1.2	1400	2513	Blue-gold tinge; adherent
2.09 Be	0.34	1.3	1400	2542	Black-blue tinge; adherent
4.23 Be	0.30	1.1	1400	2400	Black with white raised edges; adherent
1.03 Hf	0.34	1.4	1400	2673	Black with raised edges; adherent
2.22 Hf	0.34	1.4	1400	2612	Gray-black with raised edges; adherent
4.08 Hf	0.35	1.4	1400	2529	Black with raised edges; adherent
0.77 Cr	0.33	1.6	1400	2850	Black; adherent
1.63 Cr	0.34	1.9	1400	2987	Blue-gray; adherent
3.61 Cr	0.33	1.7	1400	2923	Black; adherent
0.86 Co	0.34	1.6	1285	2725	Gray-black; adherent
2.49 Co	0.34	1.7	1400	2884	Gray; adherent
3.72 Co	0.33	2.2	1400	3118	Gray-gold tinge; adherent
1.09 Fe	0.34	3.0	1300	3220	Gold-gray; adherent
1.99 Fe	0.34	2.7	1400	3335	Blue-gray; adherent
3.95 Fe	0.33	2.4	1400	3200	Gray; adherent
0.68 W	0.35	1.9	1400	2980	Black; adherent
1.96 W	0.38	14.2	1400	5787	Black with yellow adherent oxide at flaws in metal; adherent

Table 28

OXIDATION OF ZIRCONIUM-BASE ALLOYS WHICH SHOW BREAKAWAY AT 700 C AND 200 mm OXYGEN

Alloy Composition, Atom Per Cent (Balance Zr)	Slope of Log-Log Plot ^a (1/n)	Rate Constant ^b	Break-away Time (min)	Break-away Weight ($\frac{\mu g}{sq\ cm}$)	Break-away Rate ($\frac{\mu g}{sq\ cm\ min}$)	Length of Run (min)	Total Weight Gain ($\frac{\mu g}{sq\ cm}$)	Color and Character of Oxide Film
1.04 Ta	0.60	p 39.5				500	13200	Blue-black with raised edges; adherent
1.78 Ta	0.66	p 30.5				500	11600	Black with raised edges; adherent
3.54 Ta	0.60	p 26.9	270	7830	26.1	500	13000	Silver-white with raised edges; adherent
0.89 U	0.36	3.2				1400	3535	Black with raised edges; 2 faces gold flaky oxide
1.76 U	0.36	4.1				1400	3938	Black with raised yellow edges; adherent
3.52 U	0.35	3.5	530	2645	1.7	1400	4078	Black with raised yellow edges; adherent
1.08 Pt	0.34	1.5				1400	2684	Black; adherent
2.04 Pt	0.32	0.91	630	1815	2.9	1400	3225	Black with blisters; adherent
4.22 Pt	0.31	0.81	655	1763	1.8	1400	2980	Black with raised edges; adherent
1.03 Mo	0.36	2.5				1400	2492	Black with raised edges and white spots; adherent
2.34 Mo	0.35	6.5	40	1368	13.1	850	9500	Silver-gray with raised edges; adherent
3.65 Mo	0.36	3.5	64	1248	11.9	850	10200	Silver-gray with raised edges; adherent
0.96 Sn	0.28	0.92	235	1345	12.8	650	4450	Tan with black spots; adherent
1.68 Sn	0.32	1.1	111	1098	12.9	650	7100	Coral; adherent
3.60 Sn	0.29	0.49	35	596	292.0	117	13071	White; flakes off
0.58 Pb	0.28	1.1	273	1465	9.7	890	5938	Black with raised edges; adherent
1.62 Pb	0.30	1.6	34	835	15.9	580	9123	Black with raised edges; adherent
4.00 Pb	0.28	0.85	7	460	9.7	895	11165	Silver-gray with raised edges; adherent
1.42 Al	0.36	14.0	25	1467	58.9	280	14100	Ivory with raised edges; adherent
2.15 Al	0.33	12.0	24	1401	49.3	280	13683	Ivory with raised edges; adherent
3.62 Al	0.29	8.0	7	948	84.2	198	16232	Black; adherent
0.80 Si	0.40	3.2				1400	3396	Gray with white specks on faces; adherent
1.94 Si	0.43	p 2.2	115	1650	12.7	600	5921	Tan with rough surface; flakes off
3.60 Si	0.39	1.7	6	439	47.0	165	12046	Tan with rough surface; flakes off
1.01 V	0.35	4.5	530	2810	3.9	1285	5292	1 face black and 5 faces yellow and black; adherent
1.84 V	0.41	p 4.3	120	2363	6.8	1175	9195	Black with raised edges and yellow-green spots; adherent
3.88 V	0.39	496.0				675	14392	Dark yellow with raised edges; flakes off
0.65 C	0.36	2.5				1400	3256	Silver-gold with white edges and spots; adherent
1.64 C	0.41	p 2.7	48	1225	15.3	600	7400	Gold with rough surface; flakes off
3.72 C	0.46	p 4.8	23	1076	25.4	600	17500	Gray cinder like oxide; some flakes off
0.60 Nb	0.36	5.9	365	2680	5.0	875	5717	Black with raised edges; adherent
1.82 Nb	0.46	p 6.2	500	5625	7.7	875	8500	Silver with raised edges; adherent
3.82 Nb	0.35	6.7	49	1550	16.3	680	10519	Silver-black with raised edges; adherent
1.08 Ti	0.37	69.7	370	6215	9.3	930	11134	Black with raised edges and blisters; adherent
2.12 Ti	0.39	251.0	385	9468	13.0	790	14770	Black with raised edges and blisters; adherent
4.16 Ti	0.44	p 105.0	200	14450	30.2	590	26431	Black-gold tinge with raised edges; edges flake off, faces adherent

^aThis term applies only to the portion of run before breakaway.^bCubic rate law constants ($\mu g^3 cm^{-6} min^{-1} \times 10^{-7}$) unless preceded by p which signifies parabolic rate law constant ($\mu g^2 cm^{-4} min^{-1} \times 10^{-4}$). Both only apply to the portion before breakaway.

Of the 20 binary alloy systems investigated, only the copper, nickel, beryllium, and hafnium alloys showed increased oxidation resistance compared to pure zirconium.

B. Metal-Water Reactions

(L. Baker, P. Bergland, M. Kilpatrick,* R. C. Liimatainen, D. Mason, C. H. Smith, R. Warchal, W. A. Rodger and R. C. Vogel)

The experimental program to determine rates of reaction of molten reactor fuel and cladding metals with water is continuing. The principal laboratory-scale method involves the rapid melting and dispersion of metal wires in a water or steam environment by a surge current from a bank of condensers. The proposed method was presented in detail in the previous quarterly report, ANL-5896, page 101. Preliminary experience with the completed condenser discharge is reviewed in the following paragraphs. Equipment for use in the in-pile (TREAT) tests has been designed and is under construction.

1. Laboratory Studies - Condenser Discharge Method

The electrical apparatus was received during the quarter.

Four 25- μ farad condensers are charged to a maximum of 5000 volts and discharged through a one-inch long wire specimen. Preliminary work has been done with 0.030-inch diameter commercially pure aluminum wire.

One of the most important requirements of the method involves the measurement of the energy imparted to the specimen, so that the initial metal temperature may be accurately calculated. Several calorimetric cells consisting of short lengths of constantan wire (64 and 129 mils) with fine thermocouples attached were built. A current shunt was constructed according to the principles given by Park²² and used to obtain traces of current versus time on an oscilloscope. The current was found to be an exponentially decaying sine wave. Measurements of the period of the wave showed that the circuit had a total inductance of 3 μ henry. Measurements of the logarithmic decrement of current decay showed a total circuit resistance of 0.055 ohm, including 0.021 ohm in the current shunt. Heating of a typical specimen was completed in less than 300 μ seconds.

The calibration method outlined in the previous quarterly (ANL-5896, page 104) has not been entirely satisfactory with the 0.030-inch aluminum specimens, although it is believed that it will be satisfactory for

*Consultant from Illinois Institute of Technology

²²Park, J. J., "Shunts and Inductors for Surge-Current Measurements," J. Research NBS 39, 191 (1947) RP-1823

the zirconium. This resulted from the fact that the resistance of the aluminum specimens is only a few per cent of the stray resistance within the condensers and circuitry, requiring extremely accurate voltage settings. Work is continuing to improve the method of energy measurement.

Results obtained from the limited number of runs made to date are summarized in Table 29. Values for the hydrogen generated in terms of per cent of the amount expected if reaction were complete are also given in Table 29. These values were calculated from the permanent increase of pressure following each run after deducting the vapor pressure of water. The technique will be improved in future runs. The gas will be separated from the water vapor and analyzed for hydrogen in a thermal conductivity cell.

Table 29

PRELIMINARY RUNS: METAL-WATER REACTIONS,
CONDENSER DISCHARGE METHOD

Wire: 0.030-inch aluminum

Run	Volts	Hydrogen ^a Yield (cc NPT)	Hydrogen Corresponding to Complete Reaction ^a (%)	Cooling Time from Motion Pictures (millisec)	Appearance of Residue
4	2500	0	0	b	Intact
6	2800	0	0	1.4	3 large pieces
5	3000	-	-	3.9	Pieces
7	3300	4	12	2.0	Fine particles
3	3500	7	19	1.1	Fine particles
2	5000	-	-	0.5	Colloidal solution

^aData are tentative

^bNo light emitted

The cooling time given in Table 29 is the period during which glowing particles appeared on high-speed motion pictures taken of each run. Heating of the specimens occurred well within a single frame (less than 0.5 millisec); each successive frame showed a diminished intensity, so that cooling was regular and rapid with no sign of self-heating. The cooling rates were higher than anticipated; they depend upon the particle size and initial metal temperature.

The preliminary runs indicated that a variety of particle sizes were obtained, depending upon how much energy was given to the specimen. It is planned to slow the heating rate by adding inductance to the circuit in the hope that larger particles will be obtained in the more energetic runs. A better knowledge of the initial metal temperature is required before a complete interpretation of the particle size and cooling rate can be made.

The specimen of Run 4, Table 29, apparently did not reach the melting point, while in Run 2 the metal was vaporized. The production of a colloidal solution by a vaporized metal wire is similar to results reported by Plott.²³ The very rapid cooling reported here is consistent with the finding that such reactions are endothermic because of the large surface created. The rapid vaporization of metal in Run 2 was so violent that the 0.5-inch thick pyrex cell windows were shattered.

2. In-Pile Testing in the TREAT Reactor

FIGURE 28
DESIGN OF HIGH PRESSURE AUTOCLAVE FOR STUDY OF STATIC
METAL-WATER REACTIONS IN TREAT

Progress on the TREAT phase of the metal-water reaction program has been mainly on construction and procurement of equipment. A type 304 stainless steel autoclave has been designed to withstand an internal static pressure of 5200 psi at 750 F (the maximum design core temperature for the TREAT reactor). The construction of the autoclave which will be used in static tests previously described (see ANL-5896, page 112) is completed (see Figure 28).

An Autoclave Engineers valve and fittings for pressures up to 10,000 psi will be used to remove the evolved gases. The valve will be constructed of type 316 stainless steel. The packing ring material will be copper foil and graphite, which can operate at temperatures up to 1000 F. Style RI Flexitallic gasket suitable for operation at pressures up to 10,000 psi and temperatures up to 950 F will be used to seal the autoclave.

²³ Plott, R. F., "Reactions Produced by the Electrical Explosion of a Metal Immersed in a Fluid," ANL-5040 (1950).

Thermocouples (24-gauge bore platinum-platinum-10 per cent rhodium) having a response time in the order of one millisecond will be used to measure the temperature of a fuel pin and of the water. The outputs of the thermocouples are to be fed to a Honeywell Model 906 Direct Recording Visicorder Oscillograph with appropriate galvanometers.

C. Reactor Decontamination

(S. Vogler, D. Grosvenor, W. B. Seefeldt)

The present studies, which are a cooperative effort between the Reactor Engineering and Chemical Engineering Divisions, are being made to determine the feasibility of decontaminating the auxiliaries of a boiling water reactor in the event of rupture of a fuel element. The primary aim of this work is the removal of the deposited activity in situ, so that direct maintenance may be possible. A secondary, though important, objective is the study of the type and quantity of activity adsorbed and the rate at which buildup of these adsorbed activities occurs.

Four sources of material will be used for the decontamination studies:

- (1) samples of various metals that have been placed in each of two locations in the Experimental Boiling Water Reactor (exit steam line and the condenser);
- (2) portions of the EBWR system that are removed for experimental purposes;
- (3) samples of metal that have been contaminated in a loop designed to simulate operating conditions in a boiling water reactor; and
- (4) samples contaminated in laboratory autoclaves.

Laboratory autoclaves have been pressure-tested and the control system improved. A single test with non-active uranium has been completed; low levels of activity will now be introduced.

Samples of stainless steel, mild steel, and copper which were placed in the steam condenser of the EBWR during the First Defect Test were examined in the 256-channel gamma scintillation spectrometer. By means of half-life and photopeak-energy measurements, the presence of copper-64 and cobalt-58 was established. These nuclides were also found in the reactor water.

Some of the stainless steel specimens from the EBWR defect test were subjected to aqueous decontamination procedures. Because of low activity levels only qualitative judgments were made. A solution of alkaline permanganate, or a solution of permanganate and a wetting agent, followed in each case by an ammonium citrate wash, appeared promising.

1. Laboratory Static Tests

The main purpose of the autoclave tests is to obtain preliminary data on the different fission product activities which plate out on type 304 stainless steel, both in the vapor and liquid spaces. The contaminated metal may then be used for preliminary decontamination studies. Irradiated uranium metal will supply the source of radioactivity which will be limited to the millicurie level. A one to two-gram pellet of metal will be placed in 100 ml of deionized water in a 10-mil stainless steel liner in the autoclave. The autoclave will then be sealed and heated to the operating condition of 486 F and 600 psi and maintained for a given interval. After cooling, the autoclave will be disassembled and the liner measured for adsorbed radioactivity. The liner may then be utilized for decontamination testing.

The autoclaves which were described previously (ANL-5896, page 113) have been assembled and tested. Changes in the pressure-control system have narrowed the temperature and pressure fluctuations to 10 to 15 C and 15 to 20 psi, which should be adequate for these experiments.

The main portion of the system has been sealed, tested, and found to be leak-tight. The two points which cause the most difficulty are the gasket seal of the autoclave and the point at which the autoclave is joined to the line.

Initially it was planned to use a glass liner in the autoclave to contain the water and uranium. However, after an extended period of operation at 300 C and 600 psi pressure, one such glass liner was examined and found to be covered with a large amount of a white material, although the water used was deionized and had a conductivity of one micromho. Because of the failure of the glass, it was decided to use a stainless steel liner made of 10-mil type 304 stainless steel. At the completion of an experiment the stainless steel liner may be cut open and examined for deposition of uranium and fission products. The stainless steel may then be used to investigate techniques for removing adsorbed activity. One such test (using 2 g of uranium in 100 ml of water) has been completed. The autoclave was kept at 600 psi pressure for one week. Evaluation of the liner has not been completed. A second experiment, in which irradiated uranium will be used, has been planned.

2. Evaluation of Reactor Specimens

The EBWR has been operated with a defected uranium oxide fuel element.* During this operation sample coupons were in position in

*Defected uranium oxide fuel is fuel in which uranium oxide is properly canned in the appropriate material, in this case stainless steel. The cladding is then intentionally punctured, usually by drilling a small hole.

two locations of the EBWR system: in the exit steam line, and on the top-most tubes of the steam condenser. The samples from the steam condenser were examined to determine the identity of the activities which had adsorbed on the metal specimens.

During the test the reactor operated for a total power of 18,800 Mw-hr, with 80 per cent occurring during steady operation at 20 Mw from June 10 to July 11. At shutdown of the reactor, the samples of stainless steel, mild steel, and copper were removed from the condenser tubes. The stainless steel and copper samples were covered by a brown film, whereas the mild steel was pitted and streaked. The reactor was shut down at midnight and the samples were first counted at 0930 the next morning. These samples were examined in the 256-channel gamma scintillation spectrometer. By means of half-life and photopeak-energy measurements, the identity of the nuclides contributing the major portion of the activity was established. Counting was continued on succeeding days for about a week. Periodic counting was done subsequently in order to determine half-lives.

The following comments are pertinent:

1. The adsorbed activity exhibited two major peaks on all the metallic specimens; these occurred at approximately 518 and 818 kev. The counting rates for these peaks were measured as a function of time in order to determine the half-life of either or both peaks. Results are given in Figures 29 and 30.

Graphical analysis of the composite decay curve for the 518-kev peak reveals two components in each case. The half-life of the shorter-lived component was determined graphically and was found to be 14.5 hours for the activity on the copper coupon (Figure 29) and 13.5 hours for the activity on the mild steel (Figure 30). These results compare reasonably well with the reported half-life for copper-64 of 12.8 hours. Copper-64 is a positron emitter, which produces an annihilation peak at 511 kev.²⁴

²⁴Robertson, R. F. S., Private Communication

The activation product activities in the reactor water in the first defect test in the EBWR on July 11, 1958, are given as follows:

Nuclide	Activity (dpm/ml)
Sodium-24	3×10^5
Manganese-56	8×10^4
Cobalt-58	8×10^3
Copper-64	1.2×10^4

The maximum fission product activity in the reactor water was molybdenum-99, with approximately 100 dpm/ml. This may explain why fission product activities were not observed on the metal samples.

Analysis of the steam at the same time the reactor water was analyzed indicated that fluorine-18 and nitrogen-13, both with annihilation peaks at 511 kev, were the major activities.

FIGURE 29
HALF-LIFE OF 0.5I PEAK (COPPER SAMPLES)
SAMPLES OBTAINED FROM CONDENSER OF EBWR AFTER DEFECT RUN

FIGURE 30
HALF-LIFE OF 0.5I PEAK (MILD STEEL SAMPLE)
SAMPLES OBTAINED FROM CONDENSER OF EBWR AFTER DEFECT RUN

2. Based on the half-life of the 518-kev photopeak, the presence of all but trace amounts of fluorine-18 activity with a 112-minute half-life may be eliminated.
3. Following the decay of the 808-kev photopeak indicated little or no decrease in the counting rate of this peak over a period of one week. This would eliminate the presence of all but traces of manganese-56, with a 2.6-hour half-life and a photopeak at 850 kev. Because of its short half-life and the elapsed time between reactor shutdown and counting, any manganese-56 present at shutdown would be reduced by a factor of ten by the time of counting. This may account for the fact that its presence was not observed.
4. Two peaks at 511 kev and 810 kev are typical of cobalt-58 activity. The response curve of this nuclide has been measured and the ratio of peak heights (at 810 kev and 511 kev) is approximately 2.6, which agrees quite well with a value of 3.0 obtained for the unknown after six weeks of decay. After an elapsed time of 40 days, the samples were re-counted and a half-life of approximately 81 days was calculated, which compares reasonably well with the actual half-life of 71 days, especially since the calculation covered only one-half a half-life period. A difference of five per cent in the counting rate would produce a difference of about 12 per cent in the half-life calculation. These results indicate confirmation of the presence of cobalt-58 on the metal sample strips.
5. There were several other small peaks observed, some of which may be attributed to the copper-64 and cobalt-58 already identified. The others were too weak to attempt identification.
6. The activity adsorbed on the metals was rather low, so that three samples of each metal (from the same condenser tube) were counted at one time. Using only the activity found under the two major peaks (by far the major portion of the activity) the adsorbed activity per unit area may be calculated, using the earliest scan obtained approximately 10 hours after reactor shutdown. These results are given in Table 30. It appears that twice as much activity has plated on the mild steel as on the stainless steel and copper.

Table 30

ADSORPTION OF ACTIVITY ON METAL
SAMPLES IN EBWR STEAM CONDENSER
DURING FIRST FUEL DEFECT TEST

Counter: 256-channel gamma
 analyzer
 Time of Scan: Approximately 10 hours
 after reactor shutdown
 Counting
 Geometry: 50 per cent

<u>Metal</u>	<u>Adsorbed Activity</u> <u>(cpm/sq cm)</u>
Mild Steel	764
Stainless Steel	300
Copper	330

7. On both the stainless steel and the copper samples, more of the 518-kev activity was present than of the 808-kev activity, whereas the situation was reversed for the mild steel sample. These data indicate that approximately the same amount of copper-64 adsorbed on all the samples, but that a much larger amount of cobalt-58 adsorbed on the mild steel than on either then copper or stainless steel.
8. Several of the stainless steel and mild steel samples were wet ground with 80-grit paper. The results indicated that approximately 10 to 15 per cent less activity was deposited on the wet ground surface than on the as-received surface.

3. Decontamination of Stainless Steel Samples

Since the main objective of the program is to decontaminate metal surfaces, it was decided to do some exploratory experiments on the samples described in the previous section. However, because of the low counting rates, the results should be regarded as preliminary and qualitative.

The procedures tested were the following:

1.

18 Per cent sodium hydroxide	}	Heat for 30 minutes with stirring at 95 C.
3 Per cent potassium permanganate	}	Rinse with water, then heat with 10 per cent ammonium citrate for 15 minutes at 83 C.
		Rinse with water.

2. The same procedure as in 1 except that one per cent Solvadine G* replaced the 18 per cent sodium hydroxide.
3. The same procedure as in 1 except that three per cent potassium permanganate was used.
4. The coupon was treated for 30 minutes at ~ 83 C with 10 per cent ammonium citrate and then washed with water.
5. The coupon was treated for 30 minutes at ~ 85 C with a solution of 1.5 per cent tartaric acid, 6 per cent sodium hydroxide, and 2 per cent hydrogen peroxide. After treatment the sample was rinsed with water.

The results are shown in Table 31.

Table 31

RESULTS OF SEVERAL DECONTAMINATION
PROCEDURES ON EBWR SAMPLES

Procedure ^a	Counting Rate (β cpm)	
	Before	After
1	66 ^b	2
2	97	3
3	65 ^c	40
4	78	6
5	65 ^d	23

^aSee page 113.

^bThe ammonium citrate removed the brown film from the surface of the coupon.

^cThe ammonium citrate did not remove the brown film from the surface of the metal as effectively as when treated with the alkaline permanganate.

^dThis reagent did not remove all the brown film from the surface of the coupon.

The limited activity available necessitated 10-minute counting periods. Even so, the results after decontamination are so close to background that only qualitative comparisons can be made. The more effective procedures are clearly indicated.

*Salts of alkyl, aryl sulfonate - Ciba.

4. Loop Tests

The design of the loop proper is complete; construction by the shop is nearly complete. Installation in the shielded cell awaits completion of cell modification. A schematic of the loop together with general operational philosophy was presented in ANL-5858, pages 66 and 67.

D. Neutron Capture Cross Section of U^{238} (P. Kafalas and R. R. Heinrich)

The relative values of the neutron capture cross section of U^{238} for monoenergetic neutrons in the energy range 0.36 to 1.50 Mev have been determined. These values were normalized to the value in BNL-325, $\sigma = 0.130$ b at 0.360 Mev. The purpose of this work was to determine whether the small peak in the curve in BNL-325 in the region around 1 Mev is a real effect. The existence of the peak was corroborated.

Experimental Procedure

Discs of natural uranium metal (1-cm diameter, 190 mg) were supported in a reproducible position at zero degrees to the neutron "beam" of the Van de Graaff neutron generator of the Reactor Engineering Division. The neutron beam was monitored by a BF_3 counter encased in a large paraffin cylinder. This counter was at zero degrees with the incident proton beam, i.e., with the neutron "beam."

Each target was bombarded at a particular neutron energy for about

six hours. After several hours of cooling time, the target was assayed with a scintillation counter and multichannel analyzer (4 in. x 4 in. diameter NaI(Tl) crystal with 256-channel analyzer). By this time the U^{239} had decayed completely to Np^{239} . The activity due to uranium and its daughters was subtracted electronically by subtracting the radiation produced by an unirradiated uranium disc. A portion of the net gamma-ray spectrum of Np^{239} is shown in Figure 31. The region from channel 84 to channel 225 was used to determine the intensity of the 106-keV peak with its escape peak. This was used in each run to determine the relative number of capture events. (Actually the absolute number of capture

FIGURE 31
PORTION OF NET GAMMA-RAY SPECTRUM OF Np^{239}
(AFTER ELECTRONIC SUBTRACTION OF SPECTRUM DUE TO
URANIUM AND ITS DAUGHTERS)

events has been determined, but the neutron flux measurements are relative, so the cross sections which have been determined are relative values.) The efficiency of the BF_3 counter as a function of neutron energy was determined by S. A. Cox of the Reactor Engineering Division. He was also in charge of operating the Van de Graaff accelerator during these runs.

Results

The Np^{239} activity produced in each run was corrected for decay during the bombardment. The relative capture cross sections were then calculated and normalized to the BNL-325 value at 0.360 Mev. The results are shown in Table 32.

Table 32

U^{238} CAPTURE CROSS SECTIONS

Run No.	Neutron Energy (Mev)	Absolute Capture Cross Section (barn)
3	0.360	0.130 ^a
4	0.500	0.132
5	0.700	0.1385
6	0.905	0.150
7	1.100	0.156
8	1.310	0.129
9	1.490	0.126

^aNormalized value

These results are shown as solid dots along with the other points of BNL-325 in Figure 32. The results of this work corroborate the peak shown in the literature, but differ somewhat from the literature values above 1 Mev. However, BNL-325 shows only one point between 0.84 and 2.1 Mev, whereas we have determined four points in this interval. It should be noted also that the points are actually about 200 kev wide.

E. Determination of Alpha in EBR-I (P. Kafalas and R. R. Heinrich)

The study of the ratio of capture to fission cross sections has been continuing. Samples of several heavy nuclides have been sealed in aluminum capsules and are ready to be placed in EBR-I. Twenty-three samples of very pure U^{233} have been prepared from the material supplied by Oak Ridge National Laboratory. Altogether 62 samples will be placed in the reactor in order to study the vertical and horizontal patterns of capture and fission. Special fuel and blanket rods have been constructed to contain these capsules.

FIGURE 32
NEUTRON CAPTURE CROSS SECTION OF U²³⁸

V. CHEMICAL-METALLURGICAL PROCESSING

Melt refining, liquid metal extraction and intermetallic crystallization are now being examined as direct-cycle pyrometallurgical methods of processing nuclear reactor fuels.

Melt refining consists of melting the discharged fuel and holding it molten for a period of time. Decontamination is effected by oxide drossing and volatilization of rare gases and low-boiling fission products. Detailed laboratory studies of the behavior of iodine in the melt-refining process have been made. In molten uranium, isotopic mixing of fission product iodine and inert iodine added as uranium triiodide takes place rapidly and quantitatively. Iodine at EBR-II concentration level is almost completely (>98 per cent) removed from the ingot and skull after three hours at 1400 C. Volatilization of iodides of the alkaline earth and rare earth metals is the chief mechanism.

Antimony, as tracer, has been found not to be separated from uranium under nominal melt-refining conditions. The joint solubility of zirconium and carbon in molten uranium is under examination.

Two four-run series for demonstrating zirconium removal in graphite-coated crucibles were completed in the semi-works using liquation periods of three hours and five hours at 1400 C. Zirconium removals of around 50 per cent were realized from charges initially 0.7 weight per cent in zirconium. About 10 per cent higher removals were obtained with the longer liquation time. Yields for all runs varied between 90 and 93 per cent. Cerium removal, also followed in these runs, was not adversely affected by the presence of the graphite coating, being above 90 per cent in all runs from charges of 0.7 weight per cent cerium.

Melting of oxide-coated pins continues to be more difficult than the melting of massive metal. An oxide coating present on the pins serves as a diffusion barrier during exposure in the reactor. These coatings interfere with uranium coalescence in the melting operation and lower ingot yields by entrapping metal in the pouring operation. Calcium is effective in reducing the oxide, but attacks zirconia crucibles excessively. This may make necessary a pre-melting operation in an inert crucible, such as tungsten or beryllia, to effect coalescence of the uranium and provide a satisfactory charge for the melt-refining operation.

A silicon nitride, silicon carbide-impregnated graphite susceptor supplied by National Carbon Co. has shown excellent resistance to sodium vapor in three successive tests. Tungsten susceptors have also been obtained for testing.

A method proposed for processing uranium to separate the noble metals not removed by melt refining (ruthenium, molybdenum, etc.) is the Pyrozinc process. This process begins with the dissolution of the metal ingot in molten zinc. Uranium forms an intermetallic compound with zinc (U_2Zn_{17}) which can be separated by fractional crystallization. Zinc may be removed from the uranium-zinc intermetallic compound by vaporization. Uranium in the oxide dross from melt refining may be similarly recovered after dissolution in zinc-magnesium.

A number of supporting laboratory studies relative to the Pyrozinc process are being made. For example, cadmium has been suggested as an alternate to zinc in the Pyrozinc process.

A tentative phase diagram for the uranium-cadmium system is presented. It has the following features: one intermetallic compound, UCd_{11} , cubic and isostructural with (lanthanum, cerium, praseodymium) Cd_{11} and (potassium, rubidium, strontium, barium) Hg_{11} ; a eutectic between the compound and cadmium at about 0.06 weight per cent uranium at 320.8 C, peritectic decomposition of the compound at 475 C to a saturated liquid containing 2.1 weight per cent uranium and solid uranium. Cadmium-uranium solutions are containable in mild steel up to at least 550 C with no evidence of corrosion.

An electrochemical cell with the most highly purified constituents available gave potential measurements between 540 and 670 C that yield the following equation for the activity of uranium in a saturated zinc solution:

$$\log_{10} a = (-15,922/T) + 17.310 - 4.8465 \times 10^{-3} T \quad .$$

By two different sets of measurements it was shown that unsaturated solutions of uranium in molten zinc obey Henry's law to within better than 10 per cent.

Only lanthanide and actinide elements have so far been observed to coprecipitate with uranium from a zinc solution. The addition of aluminum has been shown to cause apparent precipitation of zirconium from zinc solutions.

Crystals of U_2Zn_{17} grown from solution by slow cooling through the liquidus have been shown to undergo only slight size refinement as a result of the addition of magnesium to the system. Metallic uranium reacts with liquid zinc to produce intermetallic compound crystals by a zero-order reaction whose rate varies only slightly with temperature and with the 0.83 power of the velocity of the liquid past the surface (in a turbulent flow region). The measurements can be rationalized by the assumption of a liquid film-controlled diffusion mechanism and are correlated by known engineering equations.

In the application of liquid metal processing to scrap recovery, semi-works study of recovery of uranium from crucible skulls of the melt-refining process by dissolution in a six weight per cent magnesium-zinc alloy is underway. In two runs, 80 and 90 per cent of the accountable uranium was dissolved in the zinc-magnesium solution at 800 C. These recoveries are still on the low side and need to be improved. The reduction of uranium dioxide pellets by a zinc - 6 weight per cent magnesium alloy was studied in the laboratory. After three hours the reduction was 87 per cent complete. No evidence for termination of the reaction at an incomplete stage was seen.

The distribution of fission products between uranium-zinc alloy and molten Dow-230 flux at 735 C is essentially complete in one hour. The results confirmed earlier findings that strontium and cesium are nearly quantitatively separated from uranium, while zirconium and ruthenium are left behind. Fifty per cent of the cerium and one per cent of the plutonium were also extracted.

The proposed process for recovery and purification of plutonium in reactor blanket material is molten magnesium extraction. The blanket uranium alloy composition was recently changed from the low-melting (860 C) five weight per cent chromium-uranium alloy to a high-melting (around 1130 C) three weight per cent molybdenum-uranium alloy. The magnesium extraction procedure would be more difficult to carry out at the higher temperature because of accelerated attack on materials of construction and because the operating temperature is above the boiling point of magnesium, which would make necessary operation under pressure. Alternative blanket processing methods are therefore being considered. A very promising method involves the use of zinc to dissolve the blanket alloy. Separation of plutonium and uranium from solution is effected by cooling the solution to precipitate them as zinc intermetallic compounds. The precipitated material is isolated and to it is added sufficient magnesium to form the 46.5 weight per cent magnesium-zinc eutectic composition. Plutonium is soluble in this eutectic solution, while uranium is relatively insoluble.

Available results of experiments on this process, called the Pyrozinc-magnesium process, show that plutonium is well carried (95 per cent or more) on a U_2Zn_{17} precipitate in accordance with previous laboratory work. Essentially complete solution of the plutonium and simultaneous precipitation of the uranium is effected by formation of the 46.5 weight per cent magnesium-zinc eutectic. Solubility of uranium in the eutectic solution has not been established (results ranging from 0.01 to 0.22 weight per cent) and will limit the separation of uranium and plutonium achievable. If the uranium solubility is on the high side, any further necessary separation can be achieved by a partial distillation of magnesium and zinc and phase separation.

The hydriding-dehydriding approach was again considered, since in a sense it is similar to the Pyrozinc-magnesium process. Both ultimately make plutonium available for solution in magnesium and both rely on the low solubility of uranium in magnesium for plutonium-uranium separation. However, the three weight per cent molybdenum-uranium alloy has proved to be resistant to hydriding in contrast with natural uranium which hydrided easily.

Work is continuing on application of the results of chemical-metallurgical process and development studies to design and component testing of facilities for the EBR-II fuel processing plant.

Design of the fuel cycle facility and review of architect-engineer drawings was continued. Shop prints are being prepared for the cell cranes. The radiation-resistant manipulator is scheduled for testing in January 1959. The manipulator removal "blister" was completed. The design of the protective shutters for the windows was completed. The purchase order for the windows has not yet been placed.

A working model of a remote luminaire for the argon cell was tested. The effect of gamma radiation on clear incandescent lamps was determined.

The operating characteristics of the melt-refining furnace were improved by using zirconia grain as a crucible-insulating material. Melt temperatures have been accurately estimated by indirect measurement using a reference thermocouple. Fifteen runs are described. An experiment was made to estimate the effect of fission product decay heating of the pins in the furnace crucible. The efficiency of the prototype fume trap was tested for both a heated and an unheated crucible lip.

The large number of shop prints were approved for the laboratory and service building. Design of auxiliary equipment continues. The design of the primary system for treating high-level liquid wastes was completed.

Laboratory studies are being made of fundamental thermodynamic properties of materials of interest in the high-temperature program. These include calorimetric studies of refractory hard metals and other compounds.

The purification and analysis of molybdenum disulfide, prior to a determination of its heat of formation by bomb calorimetry, have been successfully accomplished. The rotating bomb has been calibrated with standard benzoic acid with a precision of 0.03 per cent; some improvements in technique are being sought.

A nickel bomb for fluorine combustion studies has been assembled and tested. Combustions of metallic molybdenum and tungsten to their hexafluorides have been carried out with greater than 99 per cent completion.

A. Laboratory Studies
(H. M. Feder)

1. Melt Refining Studies
(N. Chellew, A. Schneider, J. Schilb)

a. Behavior of Fission Elements in Melt Refining

Iodine

In previous experiments (Runs I-44A and I-52A, ANL-5896, page 123) the effect of iodine concentration on its removal by melt refining was investigated. An increase in concentration from 0.008 to 415 ppm by the addition of uranium triiodide to irradiated uranium did not significantly change the removal of the radio-element from the uranium ingot. However, it was not known if isotopic mixing of the iodine species had occurred. Additional experiments have now provided an answer to this question and offer a more detailed picture of the quantitative behavior of iodine.

Tracer iodine-131 was obtained by irradiation of unenriched uranium pins in the CP-5 reactor with a thermal flux of 10^{12} n/(sec)(sq cm) for 72 hours followed by about 15 days cooling. Uranium triiodide was prepared by direct combination of iodine vapor and finely divided uranium (produced by hydriding and dehydriding) at 520 C in high vacuum. The product, which sublimed to a zone heated to approximately 460 C, contained 65 ± 4 per cent iodine (theoretical for uranium triiodide, 61.5 per cent). The irradiated uranium pins and uranium triiodide were placed in a hole drilled in a block of "fissium" metal and were covered with a lid of the same alloy. The charge, containing about 800 ppm of inactive iodine, was then resistance heated in a porcelain tube furnace under a static helium atmosphere to a nominal temperature of 1300 C for a total melt time of three hours. The assembly of crucible and quartz and tantalum tubes is shown in Figure 33a. When the furnace had cooled, the quartz tube containing crucible, charge, and tantalum liner was removed for inspection and analyses.

A survey of the tantalum liner with a portable GM survey meter showed relatively high activity in a zone that had been at a temperature of 425 to 575 C, as determined by a study of the temperature profile prior to the experiment; dark gray material had condensed in the same zone to form a band about $1\frac{1}{2}$ inches wide. Various portions of the assembly were separately treated with acid to recover iodine-bearing material. Active and inactive iodine analyses are given in Table 33.

FIGURE 33
ASSEMBLIES FOR COLLECTION OF VOLATILIZED IODINE-BEARING MATERIAL

Table 33

ANALYSES OF IODINE ISOTOPES VOLATILIZED DURING MELT REFINING
(Run I-62 A)

Crucible: Zirconia
Charge:^a "Fissium" alloy (312.35 g) + irradiated U (3.67 g) + UI₃ (0.4146 g)
Atmosphere: Helium (500 mm)
Total Melt Time: 180 minutes
Temperature: 1300 C (nominal)

Fraction	Inactive Iodine		Iodine-131		
	Weight ^b (mg)	Per Cent of Element	cpm ^c	Per Cent of Activity	Specific Activity ^d
Charge	255	100	1.6×10^8	100	6.3×10^5
Tantalum Liner					
Deposit Zone (425 to 575 C)	31.8	12.5	1.5×10^7	9.4	4.7×10^5
Melt Zone (~1300 C)	Non detectable		Non detectable		--
Quartz Tube					
Interior (34 to ~1300 C)	8.2	3.2	3.1×10^6	1.9	3.8×10^5

^aFinal w/o composition of charge was: I, 0.0806; Mo, 2.4; Ru, 1.9; Zr, 1.0; Rh, 0.3; Pd, 0.2; Ce, 0.7; U remainder.

^bAnalyses accurate to ± 5 per cent (relative)

^cValues corrected for decay, coincidence, and geometry. Estimated accuracy, ± 10 per cent (relative).

^dDefined as cpm of iodine-131 per milligram of inactive iodine.

A comparison of the specific activity of the charged and volatilized fractions indicates that nearly complete isotopic mixing had occurred in this experiment. Approximately 80 per cent of the volatilized iodine was found in the deposit zone. This zone contained 12 per cent of the iodine originally charged. Additional analyses of the sublimed material were made by spectrochemical, X-ray spectral, gamma-ray spectrometric, and fluorophotometric techniques. These analyses showed that: (1) barium-140, lanthanum-140, and iodine-131 together accounted for nearly all of the gamma activity; (2) no uranium and negligible amounts of the "fissium" components were present; (3) 10 milligrams of calcium (order of magnitude) was present, together with approximately one-tenth this amount of barium; and (4) other elements were found only in trace amounts.

The analyses thus reveal that iodine in the sublimate is mainly present as calcium iodide. This conclusion is consistent with thermodynamic data which show calcium iodide to be among the most stable of the metal iodides and with the physical properties of the substance (melting point, ~ 740 C; boiling point, 1200 to 1300 C). The origin of the calcium found is not known; about 20 ppm of calcium in the originally charged material would have been sufficient to react with the 40 milligrams of iodine collected during the experiment. This amount of impurity could have been present in the materials charged to the crucible.

A further experiment was made in an induction-heated melting and casting furnace to obtain additional information on the quantitative behavior of iodine. A charge containing about 600 ppm of iodine was prepared as already described. It was held at a nominal temperature of 1400 C for three hours in the assembly shown in Figure 33b. The condenser was then lifted and the melt poured. A record of the results of this experiment is presented in Table 34.

Complete isotopic mixing of the iodine species apparently occurred. The essentially complete removal of iodine from the ingot is in accord with results previously obtained in melt-refining metals with high iodine concentrations (Table 27, ANL-5896, page 125). Total iodine volatilized to the condenser amounted to roughly 17 per cent of the starting material. The total iodine accounted for was only slightly larger than this. Additional experiments are planned to determine whether the remainder of the iodine is lost by permeation through the crucible and subsequent volatilization.

Antimony

The distribution of tracer-level antimony in melt refining has been determined. Irradiated uranium diluted about six-fold with "fissium" alloy was used. The melt was heated for three hours at a

Table 34

DISTRIBUTION OF IODINE IN MELT REFINING
(Run I-67 A)

Crucible: Zirconia
 Charge^a: "Fissium" alloy (316.10 g) +
 irradiated U (3.67 g) +
 UI₃ (0.3458 g)
 Atmosphere: Helium (680 mm)
 Total Melt Time: 180 minutes
 Temperature: 1400 C

Fraction	Inactive Iodine		Iodine-131		
	Weight ^b (mg)	Per Cent of Element	cpm ^b	Per Cent of Activity	Specific Activity ^c
Charge					
Wt(g) - 320.12	197	100	2.4×10^8	100	1.2×10^6
Volatilized to Condenser	29	14.7	4.0×10^7	16.7	1.4×10^6
Ingot					
Wt(g) - 298.30	No analysis		4.4×10^5	0.2	-
Skull					
Wt(g) - 19.35	Non-detectable ^d		3.6×10^5	0.15	-
Crucible	Non-detectable ^d		2.9×10^6	<u>1.2</u>	-
Total Recovered				18.25	

^aApproximate iodine level in charge was 612 ppm. Concentrations of other "fissium" constituents are similar to those listed in Table 34.

^bEstimated accuracy of values offered in Table 34.

^cDefined as cpm of iodine-131 per milligram of inactive iodine.

^dLimits of detection, ~6 milligrams.

nominal temperature of 1300 C prior to casting. Analyses of antimony-125 present in the control, skull, and ingot were made after isolation of this activity by paper chromatography. The results of this experiment are reported in Table 35. Little or no movement of tracer-level antimony occurred.

Zirconium

Examination of the ternary zirconium-uranium-carbon system has been continued as an aid to the problem of zirconium removal in melt refining. From earlier experiments (ANL-5896, page 126) it

Table 35

DISTRIBUTION OF ANTIMONY IN MELT REFINING
(Run I-51A)

Crucible: Pressed zirconia
 Charge:^a "Fissium" alloy + ORNL irradiated uranium
 Atmosphere: Helium
 Melt Time: 180 minutes
 Temperature: 1300 C (nominal)

<u>Fraction</u>	<u>Weight (g)</u>	<u>Specific Activity (cpm/mg irradiated U)^b</u>	<u>Distribution (% of activity)</u>
Charge	305.3	4.4×10^2	-
Skull	27.6	2.1×10^2	4
Ingot	277.1	3.6×10^2	74

^aUranium irradiated to ~ 0.007 per cent total atom burn-up and cooled 1568 days. Final w/o composition of charge was: Mo, 2.0; Ru, 1.6; Zr, 0.8; Rh, 0.2; Pd, 0.2; Ce, 0.6; U remainder.

^bEstimated accuracy of analyses, ± 10 per cent (relative).

became apparent that the mechanism of zirconium removal involved the separation from the molten metal of a solid solution of zirconium carbide and uranium carbide. The present series of experiments were for the determination of the joint solubility of zirconium and carbon in molten uranium at a temperature of 1400 C. These data are useful for defining the ultimate limits of concentration of the elements when zirconium is removed from uranium alloy as a carbide. High-purity zirconium carbide powders were charged into holes drilled in uranium blocks and covered with uranium lids. In two experiments uranium charges containing 0.19 and 1.86 per cent zirconium carbide respectively were induction heated in beryllia crucibles at 1400 C for 24 hours and quenched. Melting was conducted under one-third atmosphere of helium.

Polished ingot sections from these tests were examined. At the lower starting concentration of zirconium carbide the interior metal was found to be essentially free of inclusions or precipitated material. Samples of this metal were analyzed for zirconium and carbon. Results, reported in Table 36, indicate that by carbide liquation it is possible to reduce the zirconium content of uranium metal to as little as 0.4 weight per cent at 1400 C.

Table 36

ANALYTICAL RESULTS FOR URANIUM-ZIRCONIUM
CARBIDE MELT

Crucible: Beryllia Temperature: 1400 C
Atmosphere: Helium (250 mm) Melt Time: 24.9 hrs

<u>Element</u>	<u>Composition^a</u>	
	<u>Charge Material^b</u> (ppm)	<u>Ingot Center</u> (ppm)
Zirconium	1651	380
Carbon	238	101

^a Estimated accuracy of values listed, ± 10 per cent (relative).

^b Values include 10 ppm Zr and 22 ppm C in uranium charged. Examination of ZrC by X-ray diffraction techniques indicated purity of compound to be >98 per cent.

The ingot section from the metal initially charged with the larger amount of zirconium carbide showed liquated inclusions in decreasing concentration from top to bottom. However, at the bottom a narrow zone, occupying an estimated 15 per cent by volume of the ingot, was entirely free from inclusions and contained only precipitated carbide at the grain and subgrain boundaries (see Figure 34). Preliminary determination of the zirconium concentration in each of several 0.2-sq cm areas from ingot top to bottom by X-ray spectral analysis showed an approximate 27-fold decrease in concentration and suggests a very slow liquation rate at high concentrations of solids. Analyses of zirconium and carbon concentrations in the inclusion-free area of this ingot and subsequent ones containing varying ratios of zirconium-carbon will be reported as the information becomes available.

b. Reaction of Uranium with Container Materials

Boron nitride has been tested as a possible container material for use with molten uranium. The crucible used in the experiment, fabricated from pressed boron nitride manufactured by the Carborundum Company (reported purity, 97 per cent; major contaminant, 2.4 per cent boron oxide), was outgassed at 1300 C prior to use. High-purity uranium was liquated in a helium atmosphere for 24 hours at 1300 C. Figure 35 is a photograph of the longitudinally sectioned ingot and crucible and illustrates the undercutting and apparent wetting of the

FIGURE 34

PHOTOMICROGRAPH OF VERTICALLY SECTIONED INGOT:
URANIUM - ZIRCONIUM CARBIDE MELT

Charge: Uranium (146.36g) + Zirconium Carbide (2.72g)

Test Conditions: BeO Crucible; 24 hr at 1400 C; Helium Atmosphere

Magnification 100X

boron nitride. Examination of the metal-crucible interfacial area showed no evidence of a definite reaction zone or layer. The rate of uranium contamination by boron, calculated from the volume of undercut material and verified by a boron analysis of the ingot, was 6.5 mg/(sq cm of crucible contacted)(hr). Earlier indications that boron nitride was resistant to attack by molten uranium were evidently misleading and may be ascribed to accidental formation of a protective oxide coat on the metal.

FIGURE 35

UNDERCUTTING OF BORON NITRIDE BY MOLTEN URANIUM

Uranium Charge: Impurity Concentration - 12 ppm Carbon
10 ppm Oxygen, 5 ppm Nitrogen

Melt Time: 24 Hr

Temperature: 1300 C

2. Separations by Crystallization from Liquid Metals (I. Johnson)

a. Phase Studies (A. E. Martin, R. J. Uhle, and C. Wach)

Cadmium-Uranium System

The solubility of uranium in cadmium has been previously reported (ANL-5896, page 128). A sharp break in the solubility data at about 475 C led to an investigation of the binary system cadmium-uranium

by thermal, metallographic and X-ray techniques. The results of these experiments were fitted together to yield a tentative phase diagram for the system, shown in Figure 36. The experiments themselves are reported in some detail in the following paragraphs.

The sharp break in the solubility curve (log per cent uranium versus $1/T$) at 475 C and at a solubility of 2.2 per cent uranium in cadmium could be accounted for if there were either a peritectic or a monotectic in the cadmium-uranium phase diagram at this temperature. A peritectic would involve a change in the solid phase in equilibrium with the uranium-saturated cadmium melt at this temperature, whereas a monotectic would involve the presence of a liquid immiscibility gap.

A number of cadmium alloys with from 4 to 10 per cent uranium were held for periods up to 19 days, some above and some below 475 C, and then were cooled at fairly rapid rates. Samples of these alloys were sectioned, polished, etched, and examined metallographically. Structures which developed at the holding temperature were readily distinguished from those which developed on cooling. The examination showed that alloys which were cooled from above 475 C consisted of melt plus undissolved uranium, whereas those which were cooled from below 475 C consisted of melt, cadmium-uranium intermetallic crystals, and in some cases undissolved uranium. Thus, whereas no evidence was found for a monotectic, clear evidence for a peritectic at 475 C was found. The peritectic reaction is indicated as:

where UCd_x is the intermetallic compound.

Thermal analysis of a cadmium - 10 per cent uranium melt gave a good arrest on heating at 475 C but not on cooling. It is characteristic of a peritectic reaction to show up better on heating than on cooling by thermal analysis. Thus, this is further supporting evidence for a peritectic reaction at this temperature.

In some of the alloys held below the peritectic temperature extensive growths of intermetallic crystals had occurred. It proved to be practical to isolate these crystals from the remainder of the alloy by selective leaching with a solution of ammonium nitrate. Some of these crystals were analyzed chemically with the following results:

Sample	w/o U	w/o Cd	$\frac{\text{Cd}}{\text{U}}$ Atomic Ratio
No. 1 Coarse Sample	15.96	83.8	11.12
No. 2 Coarse Sample	15.87	83.7	11.17
No. 3 Coarse Sample	16.26	82.9	10.80
No. 1 Fine Sample	18.38	80.6	9.29

The coarse crystals, ranging in weight from 0.2 to 1.0 gram, probably contained less surface oxide impurity than the fine crystals. Giving preference to the results on the coarse crystals, the data indicated the formula of the intermetallic compound to be UCd_{11} .

The density of the crystals was measured by both the buoyancy method and the pycnometer method. The observed densities ranged from 8.95 to 9.15 g/cc.

X-ray diffraction patterns of samples of the crystals were also obtained; the pattern has been indexed in agreement with the formula UCd_{11} as a cubic lattice isostructural with the known compounds (lanthanum, cerium, praseodymium) Cd_{11} .

The nature of the cadmium-uranium phase diagram at very low uranium concentrations is not as clear as that already given. If no intermediate phase exists between the intermetallic compound, UCd_{11} , and cadmium - and none has been indicated by our experiments - there would seem to be two possible forms for the phase diagram at low uranium concentrations, viz, a eutectic between UCd_{11} and cadmium, or a peritectic involving the following reaction:

The metallographic examinations of the low-uranium portions of the many cadmium-uranium alloys produced in the solubility and related studies on this system have revealed structures which appear to be eutectic, but which show enough anomalies to raise some question as to whether, instead, the observed structures could consist merely of grain boundary accumulations of fine intermetallic crystals. However, additional evidence for the existence of the eutectic was observed by thermal analysis of low-uranium alloys. A 0.2 C depression of the freezing point was obtained. This is consistent with a eutectic, but not with a peritectic. The latter would have caused a slight elevation of the freezing point.

The best estimation of the eutectic composition was obtained by extrapolation of the solubility data to the eutectic temperature. In this way a figure of 0.05 to 0.07 per cent uranium at the eutectic composition was obtained.

A check of the literature on eutectic structures showed that, when the ratio of the two constituents in a eutectic is very high, "abnormal" structures, of the type observed in this system, are usually found. This appears to remove any remaining doubts that a eutectic exists between cadmium and UCd_{11} at a low concentration of uranium.

b. Activities in Solutions of Liquid Zinc
(I. Johnson, D. Fredrickson, R. M. Yonco)

The thermodynamic properties of solutions of uranium in molten zinc have been studied by means of the electrochemical cell:

Most of the measurements have been made with a zinc solution saturated with U_2Zn_{17} . The cell reaction in this case may be written as

Thus, the measured emf of this cell (after correction for a thermal emf) may be used to compute the free energy of formation of the uranium-zinc intermetallic compound U_2Zn_{17} . From the measured temperature coefficient of this cell one may also compute the enthalpy and entropy of formation of the intermetallic compound. A cell (V) has been set up in which highly purified cell constituents were used. The dependence of the corrected emf of this cell on temperature was found to be represented (to within ± 0.18 mv) by the quadratic equation:

$$E(\text{volts}) = 1.05276 - 1.14454 \times 10^{-3} T + 3.2045 \times 10^{-7} T^2.$$

The free energy of formation of the uranium-zinc intermetallic compound is therefore

$$\Delta F_f = -72,855 + 79.207 T - 2.118 \times 10^{-2} T^2 \text{ calories/g-atom U.}$$

The activity of the uranium, a , in the saturated zinc solutions is therefore

$$\log a = -15,922/T + 17.310 - 4.8465 \times 10^{-3} T.$$

To study the behavior of the unsaturated cell two different schemes were used. In the first approach the emf of the cell was determined immediately after the temperature was raised, but before the unstirred zinc solution had appreciably altered its composition by dissolution of the solid phase. The results of a set of such measurements (cell III) are given in Table 37. In this table $N_{\text{sat'd}}$ is the mole fraction of uranium in a saturated zinc solution at the given temperature. This quantity was computed from the known solubility-temperature relation for uranium in zinc (ANL-5858, page 80). $N_{\text{unsat'd}}$ is computed on the assumption the amount of uranium has not changed in the 15 to 25 minutes required to reach thermal equilibrium at a higher temperature. The values $\gamma_{\text{sat'd}}$ and $\gamma_{\text{unsat'd}}$ were computed from the activities and the mole fractions given. The activities were computed from the measured emf's, using the equation:

$$\log a = nFE/RT$$

Table 37

ACTIVITY COEFFICIENTS OF URANIUM IN ZINC SOLUTIONS

<u>Temp (C)</u>	<u>$N_{\text{sat'd}}$</u>	<u>$\gamma_{\text{sat'd}}$</u>	<u>$N_{\text{unsat'd}}$</u>	<u>$\gamma_{\text{unsat'd}}$</u>
539.3	1.34×10^{-4}	7.05×10^{-3}	-	-
565.0	2.46×10^{-4}	1.03×10^{-2}	1.34×10^{-4}	1.13×10^{-2}
588.0	4.12×10^{-4}	1.50×10^{-2}	2.46×10^{-4}	1.50×10^{-2}
616.2	7.49×10^{-4}	2.19×10^{-2}	4.12×10^{-4}	2.19×10^{-2}
628.0	11.55×10^{-4}	2.92×10^{-2}	7.49×10^{-4}	3.11×10^{-2}

The reasonable agreement of the activity coefficients at the two concentrations for the several different temperatures strongly suggests that Henry's law holds for these solutions, i.e., the activity of uranium is directly proportional to the mole fraction.

A second method was used to examine the cell when operating in the unsaturated condition. In these studies uranium was electrolyzed out of the zinc solution by imposing an appropriate external voltage. The emf of the unsaturated cell is given by the equation

$$E = -(RT/nF) \ln \gamma - (RT/nF) \ln N_U \quad .$$

For these very dilute solutions the mole fraction of uranium, N_U , is directly proportional to the weight of uranium, W_U , dissolved in the fixed amount of zinc present. Thus, one may write

$$\begin{aligned} \Delta E = E - E_{\text{sat'd}} = & -(RT/nF) \ln \gamma / \gamma_{\text{sat'd}} + (RT/nF) \ln W_U(\text{sat'd}) \\ & - (RT/nF) \ln W_U \quad . \end{aligned}$$

Hence, if $\gamma / \gamma_{\text{sat'd}} = 1$, i.e., Henry's law holds, one should expect a linear relation between ΔE and $\ln W_U$ with a slope equal to $-(RT/nF)$ and an intercept at $\Delta E = 0$ of $(RT/nF) \ln W_U(\text{sat'd})$.

Uranium was electrolyzed out of the zinc-uranium electrode of cell III until the cell emf had appreciably increased above that characteristic of the saturated cell. After a steady, reproducible emf was attained and measured, uranium was electrolyzed into the zinc solution by shorting the cell through a high resistance. From measurements of the electrodeposition current and elapsed time the amount of uranium deposited in the zinc could be computed by Faraday's law, assuming a three-electron change and 100 per cent current efficiency. The data for this experiment, which extended over a period of four days, are plotted as ΔE vs $\log W_U$ in Figure 37. The points for experiments done on any one day lie on straight lines with the same slope. The value of n , the number of electrons involved per mole of uranium deposited, computed from the slope of these lines and the temperature is 2.87. Consideration of the estimates used in these computations indicates that sufficiently good agreement with the expected value of three was achieved. The cell had been in continuous operation for over a month when these experiments were made and consequently the electrolyte had probably become slightly contaminated. The fact that one to two milligrams of uranium was lost from solution when the cell stood overnight also suggests some contamination.

The results of both sets of experiments show that within the accuracy of the measurements the validity of Henry's law for the dilute uranium-zinc solutions may be assumed.

The cell measurements of the uranium-zinc system are now being used to prepare a paper for publication. Experimental work has been started on the cerium-zinc system.

c. Coprecipitation
(I. Johnson and K. E. Anderson)

Coprecipitation studies are directed toward understanding the factors which influence the carrying of various metallic elements, present in minor amounts, when a major metallic constituent crystallizes from a liquid metal solution. When sufficiently high solubilities exist for the minor elements, the extent of coprecipitation determines the degree of separation possible by crystallization.

A systematic experimental study of the carrying of various metals by U_2Zn_{17} crystallizing from molten zinc is well advanced. Experimental details have been given in previous reports (ANL-5858, page 76). Lanthanum, cerium, zirconium, and ruthenium have been studied in the uranium-zinc system. The results are summarized in Table 38, where the Doerner-Hoskins coefficient is given for each element. The Doerner-Hoskins coefficient, λ , is the slope of the straight line obtained when the logarithm of the fraction of minor element left in solution is plotted against the fraction of carrier left in solution.

In addition to the elements shown in Table 38, previous observers have shown that plutonium ($\gamma = 0.67$) and thorium ($\gamma \sim 1$) also coprecipitate with the U_2Zn_{17} . So far it seems that only the lanthanide and actinide elements coprecipitate with uranium. If this generalization is proved by further experiments, a separation of uranium from all but the rare earth fission elements will be possible by crystallization of U_2Zn_{17} from zinc. Separation of the lanthanide from the actinide elements by selective oxidation may, in principle, be obtained from a redox-buffered zinc solution. Addition of magnesium or aluminum to a zinc solution has been shown to control the oxidation of the uranium and plutonium.

Table 38

COPRECIPITATION BY U_2Zn_{17} FROM LIQUID ZINC

<u>Element</u>	<u>Concentration (w/o)</u>	<u>Temp Range (C)</u>	<u>λ</u>	<u>Remarks</u>
La	1.2×10^{-4} to 3.2×10^{-2}	700 to 500	0.43	Slow or fast cooling, stirring
	1.2×10^{-4} to 2.3×10^{-2}		0.57	Fast cooling, no stirring
Ce	2.4×10^{-2} to 3.0×10^{-2}	700 to 500	0.66	
Zr	8.6×10^{-3} to 1.2×10^{-2}	700 to 500	0.00	
Nb	trace	700 to 500	0.00	
Hf	trace	700 to 500	0.00	
Ru	1.8×10^{-3}	700 to 500	0.00	

Effect of Aluminum on Coprecipitation in the Zirconium-Uranium-Zinc System

Experiments reported in the last quarterly (ANL-5896, page 142) showed some difference in the apparent coprecipitation behavior of zirconium when aluminum was present. Since experiments with the system zirconium-uranium-zinc showed essentially no coprecipitation of zirconium with uranium, additional experiments were done to determine the role of aluminum.

A coprecipitation experiment was performed with 2.08 weight per cent aluminum dissolved in the liquid zirconium-uranium-zinc phase prior to the precipitation of the uranium. The Doerner-Hoskins coefficient was found to be 0.11. This compares favorably with the value of 0.10 reported on the basis of tracer experiments (ANL-5896, page 140). Thus, in both experiments a small, but significant, degree of apparent coprecipitation of zirconium was found when aluminum was added to the system.

Since the coprecipitation of a minor element with U_2Zn_{17} very likely occurs by a process of substitution of the minor element in the U_2Zn_{17} crystal lattice, it seemed unlikely that the presence of some fourth element would enhance this process. Rather, one might explain the decrease in the zirconium concentration as due to the formation of some insoluble zirconium compound with either aluminum or some impurity in the aluminum. Thus, the apparent coprecipitation would in actuality be the variation of solubility of a sparingly soluble compound.

A second experiment was done to test this hypothesis. A liquid system of zirconium-uranium-zinc was prepared at 736 C. Incremental additions of aluminum were made to this system. The liquid was stirred vigorously after each addition and sampled just prior to the next aluminum addition. The samples were analyzed for zirconium. The results of this experiment are given in Table 39.

Table 39

EFFECT OF ALUMINUM ADDITION ON ZIRCONIUM CONCENTRATION
OF A ZIRCONIUM-URANIUM-ZINC SYSTEM

Temp: 736 C
Initial Charge: Zn - 302 g; U - 3.99 g; Zr - 25.0 mg

<u>Al Added</u>	<u>Milligrams Zr/g Liquid</u>	<u>Al Added</u>	<u>Milligrams Zr/g Liquid</u>
0.0	7.35×10^{-2}	2.68	5.19×10^{-2}
0.774	6.50×10^{-2}	3.85	4.82×10^{-2}
1.66	6.31×10^{-2}	5.26	4.65×10^{-2}

These data show that the zirconium concentration in solution does decrease as aluminum is added. The fact that the first addition of aluminum did not cause a large decrease in zirconium concentration would suggest that the aluminum itself is not responsible for precipitation. Examination of the analysis given for the aluminum used showed about 99.74 per cent aluminum. The two impurities present in largest amounts were iron (0.1 per cent) and silicon (0.1 per cent). While small in absolute amount, these impurities are present in amounts comparable to the quantity of zirconium present. As a working hypothesis one may assume that the zirconium and one of these impurities react to form a sparingly soluble compound. It was then found that the data could be fitted to a solubility product form of the mass action law. However, this interpretation will be deferred until further investigations are completed.

d. Separation of U_2Zn_{17} from Zinc-Uranium Solutions
(A. E. Martin and C. Wach)

The effect of approximately two per cent magnesium on the crystallization of U_2Zn_{17} from a zinc-uranium melt during slow cooling was tested. The two comparison alloys were held at 725 C for an hour and then cooled according to the following schedule:

From 725 C to 695 C	0.5 C/min
695 C to 635 C	1.0 C/min
635 C to 420 C	2.0 C/min

Metallographic examination of polished and etched sections of the resulting ingots disclosed no great difference in size or shape of the U_2Zn_{17} crystallized. The minor variations in size and range are as follows:

<u>Alloy</u>	<u>Average Size</u>	<u>Size Range</u>
Zn - 1.96 Mg - 1.70 U	Slightly finer	10 to 600 mesh
Zn - 1.73 U	Slightly coarser	14 to 270 mesh

e. Rate of Reaction of Uranium with Liquid Zinc
(R. A. Yount)*

The rate of reaction of metallic uranium with liquid zinc has been measured and its dependence on the total time, the stirring velocity, and temperature determined. The amount of uranium reacted is a linear function of time (zero-order reaction). The reaction rate is increased by increasing the stirring speed and the temperature. A linear relation between the logarithm of the reaction rate and the logarithm of the linear surface velocity was found. The temperature coefficient of the reaction is small.

The rate of reaction was determined by measuring the loss in weight of a uranium cylinder when rotated in a crucible containing liquid zinc under a helium atmosphere. The area exposed to the molten zinc was computed from the physical dimensions of the sample prior to reaction. The rates of reaction are reported in grams/(sq cm)(sec). The specimens were 1/4-in. diameter rods of beta-randomized uranium, which were immersed about two inches into the liquid zinc.

Results typical of those used for the determination of the reaction rates are shown in Figure 38. The plots obtained do not always have a zero intercept; this is regarded as indicating that some conditioning of the uranium surface takes place during its initial immersion in zinc. The remainder of the results conform to a linear relation, i.e., a zero-order reaction. A reaction layer of crystalline intermetallic compound is always present on the specimen surface. This layer is evidently non-protective.

Figure 39 shows the variation of reaction rate with linear surface velocity (expressed as Reynold number) in the turbulent flow region. The reaction rate is seen to vary as the 0.83 power of the surface

*Resident Research Assistant from University of North Carolina - Summer, 1958.

FIGURE 38
REACTION OF URANIUM METAL WITH MOLTEN ZINC
506 C - 15 RPM
CYLINDERS 0.64 cm dia x 5 cm high

velocity. This suggested that the data might be correlated by an expression²⁵ for diffusion-controlled mass transfer of a solid through a liquid film into a turbulent (but non-vortexing) liquid, namely,

$$kd/D = 0.023 (Sc)^{1/3} (Re)^{0.83} \quad (1)$$

where k is the mass transfer coefficient, d the specimen diameter, D the diffusion coefficient of the diffusing species, Sc the Schmidt number, and Re the Reynolds number. Using known data and an estimated value for the diffusion coefficient of uranium in liquid zinc, this expression was found to fit the experimental results within their estimated accuracies.

Measurements were also carried out at three temperatures. The results are given in Table 40.

The rate does not greatly increase between 506 and 607 C. An additional test of the semi-empirical mass-transfer equation (1) may be made by computing the ratio of rates expected at these two temperatures. This may be done by using the known temperature dependence of the viscosity and density of liquid zinc and the Stokes-Einstein equation to estimate the effect of temperature on diffusion coefficients. One computes k_{607}/k_{506} to be 1.39 using the above equation. The experimental ratio is 1.38.

The rate at 707 C is, however, some 29 times greater than one would estimate by extrapolation from the results at the two lower temperatures. Examination of specimens after the experiments at 707 C showed a different type of corrosive attack.

FIGURE 39
EFFECT OF ROTATIONAL VELOCITY ON RATE
OF REACTION OF URANIUM WITH MOLTEN ZINC

²⁵Treybal, R. E., Mass-Transfer Operations, McGraw-Hill Book Co., New York, 1955, page 51.

Table 40

RATE OF REACTION
OF URANIUM WITH
LIQUID ZINC

Equipment described in
text, page 138

Rotational speed: 15 rpm
0.25-in. diam. uranium rods

Extensive pitting had occurred and evidence for undercutting of the specimen was noted. The gross mechanism of the attack at 707 C (beta uranium being the substrate) is apparently different from the mechanism of attack on alpha uranium at lower temperatures.

Further investigations will be necessary before the mechanism of the reaction can be stated with certainty.

Temp (C)	Specific Rate [g/(sq cm)(sec)]
506	5.15×10^{-5}
607	7.13×10^{-5}
707	2.6×10^{-3}

f. Chemical Reactions in
Molten Zinc
(A. E. Martin and C. Wach)

Reaction of unsintered uranium dioxide pellets with zinc - 6.12 per cent magnesium alloy was carried out on a one-pound scale at 730 C with continuous mechanical stirring under a protective cover of premelted Dow 230 flux. The progress of the reduction was followed by taking periodic samples of the melt for chemical analysis. The proportion of reactants was such that complete reduction of the uranium dioxide would have yielded a final melt of composition zinc - 5.63 per cent magnesium - 1.95 per cent uranium if there were no oxidation or other losses. The analytical data on the samples and the corresponding calculated percentages of uranium dioxide reduction are as follows:

Time of Sample (hr)	Uranium (%)	UO ₂ Reduction (%)
0.25	0.0156	0.79
0.50	0.162	8.1
1.00	0.90	44.2
2.00	1.27	62.2
3.00	1.78	86.7

As a check on the reproducibility of this reduction, a second similar reduction was made during which a single 2.0-hour sample was taken. The sample contained 1.7 per cent uranium, corresponding to a 57.1 per cent reduction of the uranium dioxide added.

A plot of the percentage of uranium dioxide reduction versus reaction time, Figure 40, reveals an apparent induction period for the first 15 minutes. The reduction was considerably slower than the rate of dissolution of uranium at the same temperature, which indicates that the reduction is not controlled by the dissolution of the uranium produced. It is uncertain

FIGURE 40
REDUCTION OF URANIUM DIOXIDE PELLETS BY
ZINC-6 12 PER CENT MAGNESIUM ALLOY AT 730 C

whether or not the uranium dioxide pellets held together throughout the reduction period. Consequently, it is difficult to estimate the surface area of uranium dioxide exposed to the melt, an important factor in a heterogeneous reaction of this type. At a later date, a more fundamental study of this reaction is planned.

g. Pyrozinc Processes
for Irradiated Fuels
(M. Ader, J. Pavlik)

Data presented in ANL-5896 indicated the feasibility of decontaminating irradiated fuels dissolved in liquid zinc via (1) molten salt oxidation and extraction of group IA, IIA, and IIIA

elements, and (2) removal of the remaining fission product metals by fractional crystallization of intermetallic compounds of the actinide elements.

The rate of attainment of a steady-state fission product distribution between zinc - 0.2 weight per cent magnesium - 1.7 weight per cent uranium and Dow 230 flux was studied in Experiment MA-Zn-49 (Table 41). Experimental conditions of this experiment were similar in all essential respects to those of the previously reported Experiments MA-Zn-44 (see ANL-5896, page 135) except that temperature was maintained at 733 to 737 C for six hours, both phases being sampled intermittently. Uranium irradiated for 1686 days, which has been cooled 372 days and which contained 95 ppm plutonium, was used as the specimen fuel. Experimental results for individual elements are given in Table 41 and are expressed in percentages to show the fraction of uranium or tracer element present in a given phase relative to the amount in the irradiated uranium charged to the melt. Decay corrections for zirconium-95 ($t_{1/2} = 65$ d), cerium-144 ($t_{1/2} = 285$ d), and ruthenium-106 ($t_{1/2} = 1.0$ y) were applied to a previously analyzed uranium control. Appropriate data from Experiment MA-Zn-44 are included in Table 41 for comparison.

The data show that magnesium is slowly depleted from solution, presumably by air oxidation, until after six hours only 60 per cent of the original concentration remains. The decrease in uranium concentration in the metal phase from three to six hours is probably due to the diminishing protection from air oxidation afforded by the magnesium. In agreement

Table 41

EFFECT OF TIME ON DISTRIBUTION OF ELEMENTS BETWEEN ZINC-
0.2 WEIGHT PER CENT MAGNESIUM AND DOW 230 FLUX

Conditions: Mullite crucible; air atm; quartz glass stirring paddle; temp, 733 to 737 C.

Nominal Comp; 2.27 kg Zn - 0.20 w/o Mg - 1.67 w/o U; 0.50 kg Dow 230 flux preheated at 725 C. Trace-level fission elements (uranium irradiated at ORNL 1686 days, cooled 372 days, 95 ppm plutonium).

Stirring Time (hr)	Magnesium in Zinc Phase (w/o)	Phase	Per Cent of Control ^a						
			U	Pu	Ce	Zr	Ru	Sr	Cs
Exp MA-Zn-49									
0.25	0.17	Metal	89	98	78	88	94	0.7	9
		Flux	0.012	0.54	21	< 1	< 0.1	33	16
0.5	0.16	Metal	93	-	-	-	-	-	-
		Flux	-	-	-	-	-	-	-
1	0.17	Metal	96	96	63	94	92	0.5	4
		Flux	0.007	1.0	38	< 0.4	< 0.04	53	35
3	0.15	Metal	99	96	55	-	-	0.4	1
		Flux	-	1.3	44	-	-	55	43
6	0.12	Metal	89	94	52	80	89	0.3	0.6
		Flux	0.009	1.4	47	< 0.4	< 0.02	52	47
Exp MA-Zn-44 ^b									
1.5	0.13	Metal	94	100	64	95	102	2.0	6.8
		Flux	-	-	-	-	-	-	-
2.5	0.13	Metal	98	97	66	94	100	2.4	7.3
		Flux	0.009	1.1	36	< 0.1	< 0.06	52	41

^aBased on analysis of irradiated uranium control of Experiment MA-Zn-44 with decay corrections applied to Zr, Ce, Ru.

^bPreviously reported in ANL-5896. Zirconium data have been revised (see text).

with other observations on the rapid rate of solution of uranium in zinc at 700 C (see section 2e), dissolution of the bulk of the uranium took place in 15 to 30 minutes.

Those elements which extract negligibly into the flux, namely, uranium, ruthenium, and zirconium, achieve their steady-state concentrations almost immediately. Those elements which extract significantly into the flux, namely, plutonium, cerium, strontium, and cesium, show flux concentrations which increase markedly between 15 minutes and one hour, and thereafter at a slower rate. For cerium these increases in

flux concentrations are matched by corresponding decreases in liquid metal-phase concentrations. For strontium and cesium, however, increases in flux concentrations are accompanied by decreases in liquid metal-phase concentrations, but, as in Experiment MA-Zn-44, material balances for both strontium and cesium are poor. It is suspected that the mullite crucible wall, the quartz glass stirrer, and, possibly, interfacial material are able to scavenge both strontium and cesium rapidly from metal solution. A portion of the scavenged activities is then slowly extracted by the flux.

For all practical purposes, extraction from the metal solution is complete within approximately one hour.

The zirconium results reported in Table 41 for Experiment MA-Zn-44 differ from those previously reported (ANL-5896). Re-analysis of all samples from experiments involving extraction of metals into Dow 230 flux at 742 C from zinc - 2 weight per cent magnesium - 1.8 weight per cent uranium (MA-Zn-43) and zinc - 0.2 weight per cent magnesium - 1.8 weight per cent uranium (MA-Zn-44) has revealed that in both instances zirconium extraction amounts to less than one per cent. Previously reported higher values were in error due to contamination by the cerium activity of gamma-counting samples prepared for zirconium assay. Revision of the zirconium results has also shown that the Doerner-Hoskins coefficient, λ , for coprecipitation of zirconium with uranium is less than the reported value of 0.07.

Experiments are in progress to determine the flux extraction and coprecipitation behaviors of uranium, plutonium, and fission products during reaction at 475 C of zinc-magnesium solution with irradiated uranium metal. Processing at this temperature (rather than by dissolution at 750 C and cooling to precipitate uranium) may be advantageous by permitting the processing of larger batches of fuel in a given-sized vessel and the use of ferrous metals as materials of construction.

Cadmium as a processing solvent is also being investigated.

h. Corrosion Studies

(1) Chromium Boride Coating (A. E. Martin and C. Wach)

Three mild steel tubes, spray-coated with chromium boride by the Norton Company, were obtained in order to test their corrosion behavior in molten zinc alloys. These tests were prompted by the

reported²⁶ resistance of such coatings to molten zinc. These tubes were one inch long and had a 3/8-inch OD and 3/16-inch ID; they were not coated on the inside. After the tube ends were sealed with a ceramic cement they were immersed in stirred, molten zinc or zinc alloys for various periods of time. The extent of the corrosion was determined by visual examination. The first test was vitiated by leakage through an end seal, which resulted in extensive interior corrosion. The results of the other two tests are as follows:

<u>Test</u>	<u>Temp (C)</u>	<u>Time (hr)</u>	<u>Melt</u>	<u>Result</u>
2	738	2	Zinc	Coating still intact
3	725	12	Zn - 6 Mg - 1.75 U	Corrosion of pin beginning

In the third test, the corrosion of the steel pin had just started after 12 hours contact. The penetration occurred at a sharp edge where the coating may have been inadvertently partially abraded during handling.

(2) Ferrous Metals in Zinc and Cadmium
(M. Ader and H. W. Lavendel)

The following alloys were tested by exposure to a stirred zinc - 0.5 weight per cent magnesium - uranium solution under Dow 230 flux at 475 to 485 C for six hours: mild (AISI 1020) steel, 410 and 430 stainless steels, Croloy 2 $\frac{1}{4}$, and GA Mechanite. The microstructures of the interfaces between the zinc alloy and the specimens were examined. For all five test materials diffusion layers produced by the solution of the ferrous alloy in zinc were present. The structures were similar to those shown by E. A. Anderson et al.²⁷ The difference in behavior between these materials apparently lies in rate rather than mechanism of attack. The materials tested are unsuitable for containing molten zinc for long periods. However, the above-mentioned paper and other literature sources point out the beneficial effects of aluminum addition to zinc and/or nitrided or other surface-coated steels. Experiments along the indicated lines will be carried out by the Semi-Works group.

Solutions of cadmium - 0.5 weight per cent magnesium containing 1 to 1.8 weight per cent uranium were stirred for 7 to 8 hours at 475 and 575 C under either Dow 230 flux or lithium chloride - potassium chloride eutectic in crucibles made of AISI 1020 steel. After cooling, the

²⁶Hodge, W., Evans, R. M., and Hoskins, A. F., J. of Metals, 7, 824 (1955).

²⁷Anderson, E. A., et al., AIME Trans., 137, 400 (1940).

crucibles were examined for evidence of attack, but none was found. To draw any further conclusions on the compatibility of mild steel and cadmium-magnesium-uranium solvent longer exposures will be necessary.

3. Thermochemistry of Inorganic Substances (W. N. Hubbard)

a. Chemical Studies (E. Greenberg)

Analytical techniques for determining the composition of samples of molybdenum disulfide are being developed. It has been reported²⁸ that molybdenum disulfide undergoes surface oxidation in air above 85 C according to the following equation:

The presence of free acid in a synthetic molybdenum disulfide sample was ascertained by making a slurry of the material in water and titrating.

In order to remove surface contaminants the sample was treated with concentrated ammonium hydroxide, washed with water, vacuum dried at room temperature, and then heated to 110 to 120 C while still under vacuum. Material treated in this manner was essentially free of surface acidity but was very hygroscopic. For convenience in subsequent handling it was decided to let the molybdenum disulfide purified in this manner equilibrate with controlled laboratory atmosphere. The calorimetric sample will therefore be analyzed for water and appropriate corrections will be applied for its moisture content.

A small sample of synthetic molybdenum disulfide, treated as described above, was analyzed for molybdenum, sulfur and impurities. Molybdenum was determined by precipitation with alpha-benzoinoxime and ignition to molybdenum trioxide at 600 C. Sulfur was determined by combustion with a vanadia-alumina-chromia catalyst²⁹ (the catalyst has since been found to be unnecessary for this combustion), absorption of the gaseous products in hydrogen peroxide and precipitation of the resulting sulfate with barium chloride. Some evidence was obtained for incomplete absorption of sulfur oxides and further work on this point is being done. Water was determined by the Karl Fischer method. Silicon was detected by spectroscopic analysis and assumed to be present as silicon dioxide. The results are summarized as follows:

²⁸ Ross, S., and Sussman, A., J. Phys. Chem. 59, 889 (1955).

²⁹ Hagerman, D. B., Faust, R. A., Anal. Chem. 27, 1970 (1955).

	<u>Per Cent</u>	<u>Theory for MoS₂</u> <u>(Per Cent)</u>
Mo	59.71 ± 0.15	Mo = 59.94
S	38.93 ± 0.22	S = 40.06
H ₂ O	1.1 ± 0.02	
SiO ₂	0.1	
Total	<u>99.84%</u>	

An additional quantity of synthetic molybdenum disulfide has been purchased from the Climax Molybdenum Company, and a calorimetric sample will be prepared and analyzed as described above. The techniques developed will also be used on the sample of molybdenite (natural molybdenum disulfide) obtained from Professor Westrum.

b. Calorimetry

(R. L. Nuttall, D. Fredrickson, J. Settle, M. Frisch*)

Molybdenum Disulfide

(M. Frisch*)

In preparing for the calorimetric determination of the heat of combustion of molybdenum disulfide, trial combustions were carried out to determine optimum conditions. These conditions should lead to complete reactions with identifiable, analyzable products. Variables under consideration are (1) size and physical arrangement of the sample of molybdenum disulfide, (2) shape and material of sample container, (3) method of ignition of samples, (4) pressure and composition of the oxygen gas mixture used in the reaction, and (5) composition of liquid phase, if any, in the bomb.

A series of trial combustions was carried out in which the completeness of combustion of molybdenum disulfide to molybdenum trioxide was gradually raised from approximately 60 per cent to over 99.9 per cent. The conditions for the most complete combustions were: (1) about a one-gram sample of molybdenum disulfide, pressed with minimal pressure into a 1/4-in. rod; (2) 0.005-in. thick platinum foil sample container, on which sample rests with only line contact; (3) a 0.006-in. platinum ignition wire in contact with an edge of the sample pellet; (4) about six times as much oxygen in the bomb as the stoichiometric requirement; and (5) presence of sodium hydroxide solution in the bomb to dissolve molybdenum trioxide and sulfur oxides.

*Resident Research Associate from University of Wisconsin.

Studies of means for obtaining all the sulfur in a well-defined state are as yet incomplete. Large variations in the ratio of sulfite to sulfate have been observed. Some encouragement is derived from observations that less than one per cent sulfite is attainable. More study is necessary on this problem.

Rotating Bomb Calorimeter

The rotating bomb calorimeter is in operating condition, although further testing and modification may be necessary. It has been used in approximately 25 runs, over half of which have been calibration experiments with benzoic acid. The other runs carried out include several trial combustions with molybdenum disulfide.

Table 42 is a tabulation of the results of one series of preliminary calibration experiments. The first column lists the weight of benzoic acid in grams reacted in each experiment. The next column lists the corrected resistance rise (ΔR), in ohms, of the calorimeter thermometer. The third column lists the Newtonian heat transfer constant (α) in reciprocal seconds. The final column lists the calibration factor ($\Delta R/g$ benzoic acid) expressed as the resistance rise per gram of benzoic acid reacted.

Table 42

SUMMARY OF CALIBRATION EXPERIMENTS WITH BENZOIC ACID

<u>Benzoic Acid</u> <u>(g)</u>	<u>Resistance</u> <u>Rise, ΔR</u> <u>(ohms)</u>	<u>Heat Leak</u> <u>Constant, α</u> <u>(sec⁻¹)</u>	<u>$\Delta R/g$ Benzoic Acid</u>
0.99988	0.178845	0.043490	0.178866
0.99801	0.178741	0.043515	0.179097
1.00192	0.179450	0.043535	0.179106
0.99976	0.179168	0.043409	0.179211
1.00145	0.179362	0.043484	0.179102
Avg			<u>0.179076 $\pm$ 0.000057</u>

The uncertainty given for the average value of the calibration factors is the standard deviation of the mean. The precision obtained is satisfactory for this preliminary series. Some improvement in precision is expected as more experience with the apparatus is acquired. The reproducibility of α , a measure of the performance of the calorimeter, that was obtained was considerably better than ± 10 per cent which is usually considered necessary.

In the course of the exploratory work with molybdenum disulfide many reduced-scale trial combustions were carried out in a Vycor reaction vessel within which the reaction could be observed. It became increasingly apparent that a transparent bomb in which full-scale reactions could be observed would be desirable. Most of the compounds to be studied here will present some problems and such a bomb would be used considerably. Consequently, a glass bomb has been designed and is being built.

High-Temperature Enthalpy Calorimeter

The design of the high-temperature enthalpy calorimeter is nearly complete. Some detailing remains to be done. Work in the shops is progressing satisfactorily on the vacuum valve, the furnace and the support unit.

Fluorine Combustion Studies (J. Settle)

The preliminary exploratory reaction studies with fluorine which have been carried out to explore the feasibility of fluorine bomb calorimetry have been encouraging. Fluorine can be made to react with most substances. In many cases the products are fluorides in single oxidation states. In a larger percentage of cases than in oxygen bomb calorimetry the products produced are gases. Although many problems have yet to be worked out, fluorine bomb calorimetry appears to be a definite possibility.

During this reporting period a pure nickel bomb was constructed, assembled and tested. Construction of the full-scale bomb charging, discharging, and analytical train was started. Further studies were made of means of supporting a sample in a bomb. The suspended foil technique (ANL-5896, page 151) in which no crucible is used, the sample being suspended from a nickel support rod, was used in the nickel bomb with samples of molybdenum and tungsten. The ignition wire was ignited electrically and, in turn, ignited the lower edge of the sample to which it was attached. Combustion of the sample proceeds upwards, most of the sample being consumed before the remaining small portion falls from the support. The combustion was 99.9 per cent complete with molybdenum and 99.1 per cent complete with tungsten, no side reactions being observed in either case.

B. Semi-Works Studies of High-Temperature Processes (L. Burris, Jr.)

1. Melt-Refining Studies

(G. A. Bennett, V. G. Trice, Jr., V. N. Thelen,
W. H. Spicer, L. F. Dorsey)

The melt-refining process consists simply of melting the fuel in a zirconium oxide crucible and holding it molten for a period of several hours at a minimum temperature of 1300 C. During this time purification from fission products is primarily effected by: (1) vaporization of the noble gases and other volatile elements, such as cesium, and (2) selective oxidation of the highly electropositive elements, such as the rare earths, and their removal in a surface skin or in a reaction layer which forms along the crucible walls. The noble metals are not removed except in a small side stream of material (called "drag-out"). This side stream, consisting largely of the crucible skull remaining after pouring the purified material, must be processed for removal of the noble metals and also for recovery of the fissionable materials. The noble metals will build up to equilibrium concentrations which are dependent on the percentage of "drag-out" material. The resulting alloys are "fissium" alloys.*

a. Studies of Zirconium Scavenging from "Fissium" Melts

As explained in previous quarterly reports, EBR-II "fissium" alloy containing two weight per cent zirconium exhibits undesirable metallurgical characteristics. A small amount of zirconium is known to be permissible (0.1 weight per cent), but the maximum permissible concentration has not yet been determined. Consequently, methods of removing sufficient zirconium to maintain an arbitrary concentration not more than 0.5 weight per cent are being developed.

*The alloy composition recently chosen for the initial EBR-II loading varies somewhat from that used in previous experiments. The two compositions are shown below:

	<u>Previous "Fissium"</u>	<u>EBR-II Loading</u>
Molybdenum	3.4 w/o	2.46 w/o
Ruthenium	2.6	1.96
Rhodium	0.5	0.28
Paladium	0.3	0.19
Zirconium	0.1	0.10
Niobium	0.01	0.01
Uranium	Remainder	Remainder

(1) Zirconium Removal through Carbide Formation
(V. Trice and W. H. Spicer)

Two series of runs have been completed to demonstrate zirconium scavenging by the liquation of "fissium" melts at 1400 C in graphite-coated zirconia crucibles. For charge material containing about 100 ppm carbon and generally between 0.3 and 0.6 weight per cent zirconium, removals were 31 to 47 per cent for three hours liquation and 44 to 58 per cent for five hours liquation. Ingot yields varied between 90 and 93 per cent.

Graphite coatings on zirconia crucibles were prepared using "Dag" 22, a suspension of colloidal graphite in an aromatic hydrocarbon. The coated crucibles were first baked overnight at 100 to 130 C and subsequently degassed at 1400 C for two hours.

The results of the demonstration series are given in Table 43. In interpreting results, both the carbon added as a crucible coating and the carbon in the charge material must be considered. Between 0.1 and 0.12 weight per cent carbon was added as a crucible coating. The data for Run 44 showed that a virgin charge (an alloy prepared in an uncoated crucible as contrasted with the carbon-contaminated product ingot of a coated-crucible run) contained about 100 ppm carbon. The carbon pickup during a five-hour liquation was about 250 ppm, for a total of 350 ppm in the product. For a three-hour liquation the carbon pickup was roughly 400 ppm. Hence, use of a product ingot for a succeeding run, such as was done in Run 38, represents introduction of carbon via the charge material (carbon concentration approximately 500 ppm). The solubility of carbon in uranium at 1400 C is 3000 ppm.

Table 43

RESULTS OF ZIRCONIUM REMOVAL RUNS

Conditions: Liquation at 1400 C for indicated times in graphite-coated crucible.
Charge: Uranium - 7.7 weight per cent molybdenum alloy, plus 0.7 weight per cent cerium metal added and indicated concentrations of zirconium.

Run	Liquation Time (hr)	Zirconium in Charge (w/o) Top/Middle/Bottom	Zirconium in Product (w/o) Top/Middle/Bottom	Zirconium Removal (%)	Cerium Removal (%)	Ingot Yield (%)	Description of Charge	Estimated Carbon Concentration in Charge (ppm)
34	3	0.60 /0.56 /0.48	0.37 /0.31 /0.19	47	94.0	91.0	Virgin	~100
35	3	0.37 /0.31 /0.19	0.149/0.133/0.124	53	96.7	93.0	Product from Run 34	~500
37 ^a	3	0.30 /0.28 /0.28	0.204/0.170/0.189	31	95.2	92.5	Virgin	~100
38	3	0.204/0.170/0.189	0.069/0.074/0.049	65	96.7	91.0	Product from Run 37	~500 ^b
40	5	0.48 /0.59 /0.58	0.34 /0.32 /0.33	44	99 +	90.0	Virgin	~100
42	5	0.31 /0.27 /0.26	0.130/0.126/0.116	56	99 +	91.5	Virgin	~100
44	5	0.34 /0.33 /0.34	0.182/0.118/0.112	58	99 +	91.7	Virgin	~80/~80 ^c
46	5	1.40 /1.42 /1.36	0.91 /0.85 /0.82	38	94.2	78.5 ^d	Virgin	~100

^aRun numbers missing were assigned to alloy preparation runs.

^bProduct from Run 38 analyzed 650 and 1300 ppm, top and bottom concentrations, respectively.

^cActual analysis of charge top/bottom; analysis of product 218/452 ppm.

^dPouring accident.

Percentagewise, zirconium removal was higher in the carbon-contaminated charges of Runs 35 and 38. However, a model of the mechanism of zirconium removal has not been postulated and tested. If the rate-limiting step is liquation of zirconium carbide from solution, it may be of little importance whether or not carbon is initially in solution or must first be dissolved from the coating.

Cerium removals were excellent in all runs and were not adversely affected by the graphite crucible coating. Cerium removals were between 94 and 97 per cent for the 3-hour runs and over 99 per cent for the 5-hour runs in which the zirconium concentration of the charge was less than 0.6 per cent. About 0.7 weight per cent cerium was added with each charge.

Furnace modifications are in progress to facilitate the study of the melt refining of plutonium "fissium" alloys. The same conditions with respect to crucible coatings and liquation time will be employed and their effect on plutonium losses noted.

(2) Zirconium Removal as Compounds Other Than Carbide
(G. A. Bennett and V. N. Thelen)

An additional run was carried out on removal of zirconium as the boride. Only 7 per cent removal of zirconium was realized from a charge initially 0.85 weight per cent in zirconium. The run was carried out in a zirconia crucible coated with a suspension of boron (in stoichiometric quantity) in oil. The oil was vaporized prior to a crucible degas at 1400 C. No further work on this procedure is planned at the present time.

b. Melting of Sodium-Coated Pins
(G. A. Bennett and V. N. Thelen)

Previous work has shown the melting of sodium-coated pins to be more difficult than the melting of uncoated pins. This is attributable, not to the sodium coating, but to an oxide coating which is present or which is easily formed on such pins from exposure to air or from oxygen present in the sodium.

The approach, suggested in the previous quarterly report, of using an oxygen-gettering agent, such as calcium in the sodium, appears unacceptable, since an oxide film is desired by the reactor engineers to serve as a diffusion barrier between the uranium and the stainless steel cartridge, thereby preventing the formation of low-melting eutectics. The addition of calcium to sodium is also undesirable since its presence would (1) create a corrosion problem with the stainless steel, and (2) reduce somewhat the heat-transfer coefficient.

Consequently, approaches are limited to reducing the oxide coatings, or reducing their interference with the pouring operation by mechanically skimming or raking them from the metal surface.

Chemical Reduction Experiments

A series of qualitative experiments was completed for the purpose of surveying various possible methods for reducing uranium oxide on pins. In these experiments, a small charge of oxidized pins, obtained by dipping in sodium at 500 C for four hours and removing the adhering sodium, was placed in the melt crucible, and the reducing agent, calcium or magnesium, was added to the crucible at various points in the melt-refining cycle. Crucibles tested were alumina, dry-pressed zirconia, and graphite-coated, dry-pressed zirconia. Blanks were run for comparative purposes. The conclusions may be summarized as follows:

1. Pin shells were present in all runs in which no reducing agent was added (blanks) irrespective of the crucible or its treatment.
2. Calcium, when used with an alumina crucible, eliminated these pin shells. The point in the melt-refining cycle at which the calcium was added had little effect.
3. Dry-pressed zirconia, either uncoated or graphite-coated, is severely attacked by calcium. The addition of barium chloride as a fluxing agent had no effect.
4. Magnesium, although contained by the zirconia crucible, is an ineffective reducing agent under the operating conditions of the melt-refining process.

Based upon the successful use of calcium in the relatively inert alumina crucible, a two-step operation, in which calcium reduction and uranium coalescence are to be effected in a stable crucible prior to melt refining in a zirconia crucible, is currently being considered.

Mechanical Experiments

An alternate method for increasing the yield in the presence of unmelted oxide or pin shells is to hold back mechanically the pin shell dross so that it will not interfere with the pouring of the metal. A possible method for doing this is through the use of a skimmer or rake. Such a device has now been fabricated. It consists of a spoon or ladle mounted in such a way that, upon tilting the crucible, a counterweight causes it to push the dross away from the pouring edge of the crucible.

Preliminary tests were carried out with this skimmer on molten lead. Qualitatively, the design appeared effective. Several different

skimmer designs are currently being developed to be fabricated from either tantalum or tungsten for use with uranium.

c. Testing of Susceptor Materials
(G. A. Bennett and V. Thelen)

During the melt-refining investigations many different materials have been considered for induction heat susceptors. Of those considered, tantalum and graphite have proved to be the most satisfactory. However, tantalum is subject to embrittlement and shows some reaction when used with Fiberfrax insulation; graphite is attacked by sodium.

To obtain additional information on the above problems, two experiments were completed during the past quarter. The first consisted of a life-time test of a tantalum susceptor, in the presence of, but not in contact with, Fiberfrax insulation (except at the upper section); the second consisted of a test in a sodium atmosphere of a silicon carbide, silicon nitride-coated Type CS graphite susceptor supplied by National Carbon Company.

The test of the tantalum susceptor was arbitrarily terminated after 91.5 hours at temperatures in excess of 1400 C. At this time the tantalum was still acting as a flux susceptor from a 4200-cps motor-generator set. During this series of runs, it was subjected to 14 heat-ups and cool-downs. Examination after final cool-down showed no cracks in either the tantalum or the weld. It was, however, badly misshapen, containing many wrinkles and indentations with a larger diameter at the lower or heated section than at the upper or colder section. It was also embrittled, and several layers of metal had flaked off the inside at the heat zone. At the upper section, where the tantalum contacted the Fiberfrax, some reaction had occurred; also, at the contact points between the molybdenum heat shield and the tantalum, welding of the two materials had occurred.

In the second test the treated graphite susceptor was thoroughly degassed and then maintained in a sodium atmosphere at a temperature of greater than 1200 C for a period of slightly over three hours. Examination of this susceptor after removal from the furnace showed it to be unattacked. Earlier tests of uncoated graphite susceptors had resulted in failure: the first, a moderately degassed cylinder, failing after 45 minutes at 400 C, and the second, thoroughly degassed, failing within an hour at 1200 C. Since the initial experiment this susceptor has been used approximately six additional times, including one run in which sodium-coated pins were melted. No evidence of attack is yet visible.

d. Irradiation Facility
(V. G. Trice)

A facility (described in ANL-5789, page 105) was installed in the core section of the CP-5 reactor to study the effect of irradiation on EBR-II "fissium" pins and to provide material for "hot" melt-refining experiments. A loading of three 10 per cent enriched pins, weighing about 70 grams each, was inserted on July 28, 1958. It is planned to irradiate these pins for about 100 days at 2 Mw and 60 days at 5 Mw. Operation of the equipment has been satisfactory.

2. Development of Blanket Processes for Recovery of Plutonium from EBR-II Blanket Material

The objective of a blanket process for EBR-II blanket material is the isolation of plutonium in sufficient purity (above 30 weight per cent) for reconstitution of core material. Fission product removal is not particularly important. Studies reported in previous quarterly reports had been made on the magnesium extraction process which consisted of several successive liquid-liquid batch extractions of plutonium into magnesium from a relatively low-melting, five weight per cent chromium-uranium alloy. Subsequently, the magnesium would be vaporized, leaving behind a relatively pure plutonium product.

In the reactor, the low melting point of a five weight per cent chromium alloy is a disadvantage, and although it might be usable, a higher melting point alloy (three weight per cent molybdenum in uranium) has been chosen for initial use. The melting point of this alloy is about the same as that of uranium. This means that the magnesium extraction operation would be a pressurized operation since magnesium boils at 1106 C. Pressure extractions will be done to establish the feasibility of such operations. At the same time, additional emphasis is being given to the pyrozinc-magnesium process - a lower temperature process which can accommodate a variety of uranium alloys.

a. Application of Pyrozinc-Magnesium Process to Blanket Materials

(I. O. Winsch, P. Nelson, J. DeKany, F. Mertes, R. Paul)

In this process (see schematic diagram in Figure 51, ANL-5896) zinc is used to dissolve the blanket material. On cooling, U_2Zn_{17} precipitates and carries down the plutonium. After a separation of the excess zinc from the uranium and plutonium compounds, enough magnesium is added to to the U_2Zn_{17} and Pu_2Zn_{17} to form a 54 weight per cent zinc - 46 weight per cent magnesium eutectic which decomposes the intermetallic uranium and plutonium compounds. Plutonium is soluble in the eutectic,

while uranium is only slightly soluble (0.24 weight per cent at 800 C) and settles out. A separation of the eutectic phase from the insoluble uranium is necessary, after which distillation is employed to separate the plutonium from the magnesium and zinc.

Two additional runs following the Pyrozinc-magnesium process have been completed. The first of this series of runs was reported in ANL-5896, page 160. Complete data on the three runs are shown in Table 44. The data are shown schematically in the flow diagrams in Figures 41, 42 and 43. Complete dissolution of the charge was realized at 800 C, as indicated by the good plutonium and uranium material balances for Experiments 2 and 3. The plutonium in the zinc supernatant solution does not represent a loss, since this material may largely be recycled.

Table 44

RESULTS OF PYROZINC-MAGNESIUM PROCESS EXPERIMENTS

Charge: 1% Pu-U Alloy - ~70 g in Exp 1 and 2, ~30 g in Exp 3
(See Figure 51, ANL-5896 for a schematic diagram of the process)

Step	Per Cent of Charge								
	Experiment 1			Experiment 2			Experiment 3		
	U	Pu	Decanted Phase	U	Pu	Decanted Phase	U	Pu	Decanted Phase
Dissolution at 800 C to produce ~3.5 w/o solution	No samples taken			96	98.8	--	97	99.2	--
Ppt by cooling to 550 C (Exp 1) and 450 C (Exp 2 and 3): Supernatant sample (represents value for perfect phase separation)	1.37	7.5	--	1.02	5.7	--	0.65	2.2	--
Decanted zinc	1.11	6.1	75	0.72	4.0	64.5	0.24	0.89	37.2
Mg addition-mixing at 800 C (supernatant sample)	No samples taken			10.2	98	--	14.3	99	--
Cooling to 450 C to ppt U (supernatant sample, values adjusted for perfect phase separation)	2.3	80.5	--	4.1	96.5	--	1.04	62.5	--
Decanted Zn-Mg eutectic, 450 C	2.1	72.5	89	1.7	40	41.5	0.8	47.2	75
Mg wash - mixing at 800 C	0.2	8.0	--	No sample			No sample		
Cooling to 670 C and decantation	0.17	9.2	88.5	0.15	27.2	70	0.22	12.3	58.5
Values adjusted to perfect phase separation	0.19	10.4	100	0.21	38.8	100	0.37	21.0	100
Heel	93.5	1.85	11.5	93.5	26	30	95.5	39.0	41.5
Material balance on decanted phases plus heel	96.88	89.65		96.37	97.2		96.76	99.39	

Over-all uranium and plutonium material balances of better than 96 per cent, with one exception (90 per cent), are good. High plutonium recoveries are possible, as shown by the high percentage (~100) of plutonium found in the magnesium-zinc phase before cooling.

FIGURE 41

PYROZINC-MAGNESIUM SEPARATION PROCESS: RESULTS OF EXPERIMENT 1

FIGURE 42

PYROZINC-MAGNESIUM SEPARATION PROCESS: RESULTS OF EXPERIMENT 2

From the uranium concentration at the decanting temperature, the final uranium-plutonium product composition may be calculated, assuming a charge composition of one weight per cent plutonium. From the values obtained, plutonium product concentrations would have ranged from 20 to 50 weight per cent. The high value is more indicative of product concentrations achievable than the low. The low concentrations indicate imperfect phase separation and some carry-over of uranium. If necessary, the plutonium product concentration can be increased considerably by partial distillation of the magnesium-zinc phase. Any necessary further separation may be achieved by partial distillation of the magnesium-zinc phase followed by phase separation.

Phase separations by decantation were erratic and often poor. Since phase separations have an important influence on product purity and recovery, it will be necessary to improve decantation techniques or investigate other methods of phase separations.

Although the preliminary results are promising, anomalous plutonium behavior occurred in three instances. In the third experiment the amount of plutonium in the eutectic solution on cooling decreased from 99 to 62.5 per cent of the amount charged. This did not occur in the first two experiments. In the second and third experiments the washes were only partially effective in reducing the plutonium content of the heel,

indicating either inadequate mixing or some type of plutonium precipitation. For example, removal of plutonium from magnesium solution by precipitation in the quantities required to explain this behavior could be effected by as little as 0.005 gram of carbon.

Further demonstration runs on this and other versions of this process will be continued.

b. Application of Hydriding Process to Uranium - Three Weight Per Cent Molybdenum Alloy
(I. O. Winsch and R. Paul)

The Pyrozinc-magnesium process is in essence a method whereby plutonium is made available for solution in magnesium. Consideration has been given to an alternative scheme consisting of the hydriding of blanket fuels followed by a dehydriding step to make plutonium available for leaching with molten magnesium. After solution of the plutonium in magnesium, the magnesium phase would be separated from the uranium metal. A subsequent distillation of the magnesium from the magnesium-plutonium phase would separate these two metals.

The hydriding characteristics of a uranium - 3 weight per cent molybdenum alloy were investigated. The alloy was heated to 240 C and held under hydrogen at a pressure of 780 mm for a period of over three hours with little reaction. Under these conditions, unalloyed uranium was hydrided to completion quickly and easily. When the temperature was raised to 300 C, there was a slight indication of hydrogen reaction with the alloy. The alloy was then heated to 400 C under vacuum to decompose any hydride which might have formed.

Only a small fraction of the alloy was converted to powdered metal. The loose metal was rather flaky and was not pyrophoric, as is the case with uranium powder. Observations made during this experiment indicate that the uranium-molybdenum alloy will not hydride under the same conditions as uranium. Additional research will be necessary to determine the kinetics of the reaction of hydrogen with uranium-3 weight per cent molybdenum if hydriding is to be applied in processing this type blanket material.

c. Irradiated Tin as Simulant for Plutonium in Distillation Studies
(P. Nelson)

Irradiated tin has been proposed as a simulant for plutonium in experiments to show the feasibility of recovering plutonium from dilute magnesium solutions by volatilization of the magnesium. As in the case of plutonium, tin is soluble in magnesium and in uranium which would be present

in an appreciable quantity because of its solubility (0.03 weight per cent) in the comparatively larger amount of magnesium. Tin is also similar to plutonium in that it will melt below the temperature at which the distillation will be performed, but it will not volatilize because of its low vapor pressure (less than 1 mm mercury at 1500 C for pure tin).

The tin will be irradiated to facilitate the analytical determinations. However, about 10 per cent of the activity is due to antimony-125 formed as a daughter product of tin-125 which is formed during irradiation. While antimony is more volatile than tin, it is expected to remain almost quantitatively with the tin at temperatures below 900 C and pressures of about 100 mm mercury. In a distillation experiment part of the antimony activity was removed from an irradiated tin sample by adding 5 weight per cent natural antimony and heating to 1150 C at 65 microns pressure. A larger amount of antimony activity could probably be removed by operating at lower pressure or higher temperature, but this seems unnecessary.

d. High-Temperature Magnesium Circulating Loop
(J. DeKany)

An experimental loop is being designed for circulating liquid metals such as magnesium at temperatures up to 950 C in order to obtain dynamic corrosion data on the tantalum container and to determine the operating characteristics of an ac electromagnetic liquid metal pump and an electromagnetic liquid metal flowmeter in such a system.

The loop design is shown in the accompanying schematic diagram (see Figure 44). The container material is tantalum. However, since tantalum oxidizes and embrittles in the presence of air at temperatures above 300 C, the entire loop will be enveloped in Inconel and the annulus between the two materials will be filled with helium gas. The sections of smaller diameter will be constructed from 20-mil, one-half-inch tantalum seamless tubing enveloped in one-half-inch nominal schedule 40 Inconel pipe, while the sections of larger diameter will be fabricated and seam welded from tantalum and Inconel sheet. All connections will be welded.

The loop is to be heated and maintained at 950 C by means of a heating transformer constructed such that the loop itself is a one-turn secondary winding whose resistance changes with temperature. The temperature of the secondary magnesium circuit can be controlled by varying the voltage upon the transformer primary.

Circulation of the magnesium will be effected by a General Electric ac electromagnetic pump with a specially designed pump cell. These have been built and received. The cell is fabricated from one-inch, schedule 40 Inconel pipe with a one-inch ID x 0.020-inch wall tantalum

FIGURE 44
LIQUID MAGNESIUM CIRCULATING LOOP

liner. In the flattened region of the cell, adjacent to the welded flexible nickel electrodes, the tantalum has been spot welded to the Inconel pipe to provide good electrical contact and allow current to flow through the fluid being pumped. The pump has been designed for a flow rate of 10 gpm against a 20-psi head. The flow rate will be measured by an electromagnetic flowmeter and recorded on a strip chart recorder.

A sampling tube has been provided to enable the withdrawal of magnesium samples at various time intervals. The sampling tube also allows the immersion of corrosion coupons into the liquid metal stream. Construction details of the sampling tube are shown on the diagram. The liquid metal samples are taken by inserting a Vycor tube through the swagelok fitting at the end of the sampling tube and withdrawing a small amount of the liquid metal.

The loop is now in construction and will be completed in the next quarter.

e. Corrosion of Various Materials in Magnesium
(R. Breyne, W. Seefeldt)

Two iron-base alloys and tantalum have been tested in molten magnesium at 800 C and 950 C. The corrosion specimens were 0.25-inch OD rods. These were rotated in order to prevent effects that might be attributable to stagnant melt conditions. Earlier tests were made in sealed capsules with no agitation at higher temperatures (ANL-5494, pages 71 to 73). Argon atmospheres were maintained in all cases. Results are tabulated in Table 45.

Table 45
NON-STAGNANT CORROSION TESTS OF SEVERAL METALS IN MOLTEN MAGNESIUM

Specimens: 0.25-inch OD rods

Run	Metal	Temp (C)	Time (days)	Rotation Rate (rpm)	Wt Change (mg)	Calculated Dimensional Change (mils ^a /day)	Measured Change in OD (mils)	Visual Examination
HT-1	SS446	800	1	144	-90	0.3		Severe local attack
HT-2	Croloy 2 $\frac{1}{4}$	950	1	144	-310	1.1		Severe local attack in bottom 1 inch; some broad pits above 1 inch; grains evident in regions of general attack.
HT-5	Tantalum	950	9	144	+188		+1.7	Yellow surface layer; reasonable adherent; some cracking.
HT-5A	Tantalum	950	21 (30 days total)	144	21		0	Same layer evident as in HT-5, but some additional cracking. No subsurface attack evident.
HT-6	Tantalum	950	21	288	+26		0 to +10	Yellow surface layer having cracked appearance.
HT-7	SS446	950	1	144	-796	2.7	-4.7 to +1.3	Severely roughened; little interface effect.
HT-8	SS446	800	5	144	-416.5	0.3	-2.7 to +3.5	Uniformly roughened; no obvious interface effect.

^aBased on submergence of 3 inches; area: 14.2 sq cm; also assumes change is proportional to time.

The iron-base alloys tested, Croloy 2 $\frac{1}{4}$ and stainless steel Type 446, suffered severe local attack in the liquid phase. This effect was greater at the higher test temperature. Any interface effect appeared to be well masked by the severe local attack in the liquid. This contrasts with the results of the earlier stagnant tests with Type 446 stainless steel, where liquid-phase corrosion was uniform and interface corrosion very severe. The local attack observed was estimated to extend to depths of 15 mils (one surface) compared to maximum average OD changes of 4.7 mils (two surfaces). On the basis of these tests it appears that the two alloys tests have limited usefulness even at the lower 800 C temperature.

Two tantalum rods were subjected to 950 C magnesium for 30 days and 21 days. A yellowish surface film formed on both specimens. Though reasonably adherent, the film did contain a large number of cracks visible with a microscope. A successful method to remove this film was not found, and weight losses shown in Table 45 are not on a bare metal basis. A micrograph of a cross section of the film plus base metal is shown in Figure 45.

In an effort to characterize the film, spectrographic analyses were obtained on a sample of the corrosion rod from Run HT-5A. One analysis was made directly on the film, a second on a fresh cross section of the tantalum rod containing no film. The results are shown in Table 46. Other than tantalum, it appears that aluminum, magnesium, and manganese are the major constituents of the film. It was not possible to determine the relative contents of these with tantalum content. The

Figure 45

CROSS SECTION SHOWING SURFACE
FILM FORMATION ON TANTALUM
AFTER EXPOSURE TO
MOLTEN MAGNESIUM

Temperature: 950 C
 Time: 30 days
 Magnification: 100 X

Table 46

SPECTROGRAPHIC ANALYSIS OF SURFACE
FILM ON TANTALUM AFTER EXPOSURE
TO MOLTEN MAGNESIUM

Sample: HT-5A
 Exposure: 30 days, 950 C, 144 RPM

Element	Relative Intensity ^a	
	Area With Film	Area Without Film
Al	50	T
Ca	1	0.3
Cr	1	-
Fe	8	T
Mg	20	0.3
Mn	20	0.3
Ta	VS	VS
Ti	8	-
V	2	-
Zr	1	T

^aNo units of any kind have been assigned to the values reported; numbers are relative only and accuracy is factor of two. T denotes trace; VS very strong.

titanium and vanadium contents are thought to be due to impurities from the graphite. The latter was used to contain the molten magnesium. Further efforts at characterization of this film will be made.

The tantalum showed little dimensional change, and no intergranular attack was observed metallographically. Doubling the speed of rotation in Run HT-6 had no observable effect. It appears that tantalum is useful in this environment up to at least 950 C.

3. Uranium Purification through Processing in Liquid Metal Solution

Pyrozinc Process

This is a process by which uranium recovery and purification may be effected by dissolution of uranium and its alloys in zinc followed by cooling to crystallize out of solution a uranium-zinc intermetallic compound, U_2Zn_{17} . This compound can also be produced directly at a low temperature by reaction of uranium with zinc (see page 137). The supernatant or excess zinc solution which contains the bulk of the fission products is removed from the U_2Zn_{17} crystals. These are retorted to drive off the zinc, and the uranium is subsequently coalesced by heating to above its melting point.

a. Application to "Drag-Out" Processing (E. J. Petkus, E. F. Johnston)

A small portion of the metal from the melt-refining process must be removed and processed for noble metals separation in order to limit their buildup in recycled fuel. This small portion will consist largely of crucible skulls, which necessarily must be processed for recovery of the contained fissionable material. The Pyrozinc process is being investigated for this purpose.

"Fissium" skulls and slags from experimental melt-refining runs are being dissolved in a zinc-6 weight per cent magnesium solution to establish uranium recoveries and conditions required for effecting maximum recovery. The magnesium is added to reduce uranium oxide present in the skulls and slags which were produced in melt-refining runs made for study of zirconium removal as the carbide. Considerable carbon is undoubtedly present as a result of additions made for zirconium removal.

Eighty and 90 per cent of the contained uranium was recovered in two dissolution runs. These are considered on the low side and improvement will be sought. The skull material was contacted twice (each time at 800 C for two hours) with the 6 weight per cent magnesium-zinc alloy because of volume limitations of the apparatus. The zinc

solutions were sampled and filtered at 800 C. No difficulty in the high-temperature filtration was encountered. The residue remaining after the zinc dissolution was dissolved in nitric acid, and the final solution was analyzed for uranium. This, together with the zinc solution analyses, yielded the total amount of uranium present.

In the above runs the skulls and slags were removed from the zirconia crucibles for dissolution. In future work, processing of the skulls in place in the melt-refining crucible will be carried out, and equipment for this purpose is being constructed.

b. Development of Engineering Techniques
(E. J. Petkus, E. F. Johnston, L. Steenberg and
L. F. Dorsey)

In the Pyrozinc process engineering methods suitable for remote operation are required for the solid-liquid phase separations and the retorting operations.

Physical Removal of U_2Zn_{17} Crystals

Crystals of U_2Zn_{17} may be settled onto a graphite dish by means of cooling and stirring (ANL-5858, page 115). The crystals may then be removed from the solution by lifting the graphite dish out of the solution. The first experiments were done with no provision for drainage of excess zinc. Thus, the separation involved overflow of zinc solution during the raising of the dish. The dishes were later modified to include drainage holes in the bottom. Analysis of the mother liquor, after reheating to dissolve any U_2Zn_{17} present, indicates the effectiveness of separation. Analytical data received for an overflow run showed a uranium recovery efficiency of 75 per cent. In this run the dish was completely filled with crystals and some uranium was lost by overflow. The U_2Zn_{17} cake in the tray contained 18 weight per cent uranium. (This compares with a theoretical uranium concentration of 30 weight per cent, and values of around 20 per cent achieved by filtration.) This type of operation would necessitate careful calculation of volumes and accurate density data to achieve both high uranium recovery and a low zinc content in the cake.

In another run 20-mil holes were drilled in the bottom of the dish. The uranium recovery was 49 per cent, the uranium content of the U_2Zn_{17} cake being 17 weight per cent. There was definite evidence of drainage through these holes, since the metal level was below the lip of the dish. The low yield is probably the result of loss of some U_2Zn_{17} crystals through the holes, although conditions were reasonably conducive to growth of sizable crystals (cooling of 0.55 per cent uranium solutions from 725 to 500 C in 2.5 hours).

Although recoveries in the above two preliminary tests were poor, the basic idea of removing the crystals from solution is considered sound. Therefore, other similar devices will be tried such as the use of a basket fashioned from tantalum or tungsten wire mesh. In addition, removal of the solution instead of the crystals will be attempted by decantation and siphoning.

Zinc Vaporization

The vaporization of zinc and its collection in a suitable form remote from the uranium is under investigation. A new condenser, illustrated in Figure 46, was designed and tested. It consists of a stain-

FIGURE 46
ZINC VAPORIZATION APPARATUS

less steel cone mounted above an alumina crucible, all contained within a Vycor tube for operation under vacuum. Vaporized zinc flows up through a zirconia baffle, condenses on the cone, and flows down the cone into the reservoir. A thermocouple is attached to the cone to record the course of the vaporization. A boron nitride coating is used in the zinc reservoir to prevent interaction of zinc with the stainless steel.

The apparatus operated satisfactorily in a run using pure zinc as the charged material. Five hundred grams of zinc was vaporized under vacuum at 800 C for two hours. Ninety-eight per cent of the charge

was collected in the condenser. The crucible was completely devoid of zinc.

Satisfactory operation of this apparatus for small-scale work is encouraging, and consideration is now being given to design of larger-scale, remotely operable units.

Boron Nitride Protective Coatings

The wetting of graphite crucibles by 6 weight per cent magnesium-zinc solutions prompted the trial of boron nitride powder as a mold release agent. A slurry of equal parts of boron nitride powder and water was made and painted on the inside of a graphite crucible. After vaporizing the water vehicle, a 6 weight per cent magnesium-zinc solution was held in the crucible for one hour. Upon cooling the ingot was easily released from the mold. A test on a larger scale was not successful, possibly because of improper coating technique or washing away of the coating by the large volume of melt.

The boron nitride slurry was also used as a protective coating on the inside of a Pyrex sample tube. A uranium-magnesium-zinc melt was drawn up into the sample tube and cooled. No spalling of the glass occurred during cooling and the sample broke cleanly away from the glass. No reaction of the melt with the glass was evident, in contrast with samples taken in uncoated tubes which were covered with a dark reaction layer.

C. Fuel Processing Facilities for EBR-II (J. H. Schraidt)

1. Process Auxiliaries and Building

The Fuel Cycle Facility (formerly designated the Process Building) for the processing of EBR-II fuel has been described in previous quarterly reports (ANL-5789 and ANL-5820). The architect-engineer is the H. K. Ferguson Company, Cleveland, Ohio. A number of drawings have been received from the architect-engineer for review, including the following:

1. Transfer lock mechanism between the argon cell and the air cell.
2. Fuel coffin transfer carriage.
3. Structural steel for building.
4. Reinforced concrete.
5. Ventilation flow diagram.

a. Cranes and Manipulators (J. Graae)

The basic design of the 5-ton cranes for the argon cell and air cell has been reviewed with Paceco (Pacific Construction and Engineering Co.) which is now engaged in preparing shop drawings.

A total of 365 drawings have been prepared by General Mills, Inc., for the radiation-stable manipulator; 210 of these drawings have been approved and released to the General Mills shop for manufacture. The manipulator is scheduled for completion and testing in January, 1959, about two months later than previously scheduled, because the process of approving drawings has been more time-consuming than General Mills, Inc., expected.

Since the design of the General Mills, Inc., prototype manipulator bridge has been approved, we are using this design for laying out the two manipulator bridges in the air cell and the power and control pick-up system for both cranes and manipulators. Effort is being made to arrange a layout of the bridge rails which will allow the manipulator arm and the crane hook to approach the cell walls as closely as possible.

b. Shielding Windows
(J. Graae)

The design of the shielding shutters for the shield windows was completed. The shutters are closed when a window is not used for observation purposes. This is necessary at the anticipated gamma radiation levels to increase the installed life of the window glass to a practical level.

The purchase order has not yet been placed for these windows, and evaluation of the bids submitted by the vendors has not yet been completed.

c. Cell Lighting
(T. W. Eckels, L. F. Coleman and P. Kelsheimer)

Mercury-vapor lamps, 1000 watts, will be used for lighting in the air and argon cells. These will be designed for remote installation and removal. A working model of a 1000-watt mercury luminaire was constructed and satisfactorily installed and removed with a manipulator. The construction details of the wall mounts and the selection of a radiation-resistant electrical insulation for the lamps remain to be worked out. Tests are planned to check the characteristics of gamma-irradiated mercury lamps.

An experiment was conducted to determine the effect of gamma darkening of glass upon the light intensity emitted by lamp bulbs. Clear glass, 100-watt incandescent lamps were irradiated in the Argonne Gamma-Irradiation Facility. The experimental data are given in Table 47.

The results show that a 100-watt lamp lighted while being irradiated for four hours at a gamma dose rate of 1×10^6 roentgen/hour, the expected maximum gamma-dose rate for the Fuel Cycle Facility, would

Table 47

LIGHT EMISSION FROM GAMMA-IRRADIATED INCANDESCENT LAMPS

Clear glass, 100-watt incandescent lamps were irradiated in the

Argonne Gamma-Irradiation Facility.

Lamp A was irradiated unlighted for tests 1 through 5.

Lamp B was irradiated lighted for tests 1 through 5.

Lamp C, the control lamp, was not irradiated.

Temperature within an irradiation urn with the lamp lighted was 40 C.

Rads $\approx$ roentgens $\times$ 0.83

Test No.	Irradiation				Post-Irradiation Tests				
	Time (hr)	Test Dose (rad)	Cumulative Dose (rad)	Time Lamp Lighted (min)	Lamp A		Lamp B		Lamp C
					Elapsed Time Since Removal from Gamma Field (min)	Light Emitted (% Original)	Elapsed Time Since Removal from Gamma Field (min)	Light Emitted (% Original)	Light Emitted (% Original)
Before Irradiation	0					100		100	100
1	3.8	4.3×10^6	4.3×10^6	0.5 5 8	5.5 10 13	48 70 72	14.5 19.0	84 85	
2	16.6	1.9×10^7	2.3×10^7	0.5 5 10	5.5 10 22	41.5 62.0 73.0	11.5 16 28	79.5 83 90	100
3	5.7	7×10^6	3.0×10^7	0.5 5 8	5.5 10 13	48 71 73	14.5 19 22	83.5 84 85	100
Before Irradiation	(~50 hr annealing)					80		89	100
4	51.4	4.87×10^7	7.9×10^7	0.5 5 20	5.5 10 32	44.5 61 73.5	11.5 16 48	84.7 86.5 88.5	100
5	64.3	5.7×10^7	1.36×10^8	0.5 5 20 25	5.5 10 32 54	42.5 66.4 74.2 75.8	11.5 16 48 60	84 85 87 87	100

emit approximately 90 per cent of its normal initial light. Another lamp, not lighted during the four-hour irradiation period, would emit only 45 per cent of its normal light when turned on. However, in less than 24 hours of operation its output would recover to the same 90 per cent as the first lamp. Up to the limits of this test (142 hours of exposure or 1.4×10^8 roentgen integrated) the lamps would continue at the 90 per cent output.

Additional tests are planned to establish the time required for the recovery of a heavily gamma-darkened unlighted lamp after being turned on while still in the gamma field. In a post-irradiation test of a gamma-darkened lamp, 65 per cent of this recovery takes place in the first 20 minutes of operation. The recovery time in the gamma field is expected to be about the same.

2. EBR-II Fuel Processing Mock-Up Facility

a. Argon Cell Mock-Up (D. C. Hampson)

The installation of the manipulator removal "blister" was completed. Final testing of the operation of the "blister" will be done in January, 1959, when the prototype circular operating manipulator is installed.

b. Melt-Refining Furnace (A. A. Chilenskas, M. A. Slawewski, T. F. Cannon)

The operating characteristics of the furnace have been improved through the use of insulating zirconia grain (Norton Type I) as a material of insulation for the melt crucible. The reduction in the crucible heat losses has resulted in reducing the required power input and in lowering the coil temperature (see Table 48). The crucible insulation (Figure 47) consists of a $5/8$ -inch thickness of insulating zirconia grain confined in a fused silica (Amersil*) sleeve. A $3/8$ -inch thick wall tantalum susceptor, on order, will replace the temporary graphite susceptor presently in use. Graphite is subject to attack by sodium and some fission product fumes.

It is planned to determine the melt temperature indirectly by measuring the temperature of a boron nitride block placed in contact with the melt crucible susceptor. This method of temperature measurement eliminates the need for an immersion thermocouple in the melt. The boron nitride block is $1\frac{1}{2}$ inches in diameter and about $1\frac{1}{4}$ inches in length. The top face of this block is in contact with the bottom of the susceptor. The thermocouple is located in a hole drilled from the bottom of this block to

*Product of Englehard Industries, Inc. Amersil Quartz Division,
Hillside New Jersey

Table 46

SUMMARY OF MELT-REFINING FURNACE RUNS

Runs were made with zirconia crucible insulated with insulating zirconia grain (Norton Type I) confined in a fused silica sleeve (Amersil).
 Melt temperature measured with a platinum-rhodium thermocouple.
 Reference thermocouple, chromel-alumel, insulated with a cylindrical block of boron nitride placed in contact with the bottom of susceptor.
 Number of furnace coils, 1 2-inch diameter solid copper -- 5.
 Induction furnace power rating -- 30 kw.

Run No.	Power Input (kw)	Temperature of			Charge			Crucible Cover
		Coil (C)	Melt (C)	Ref ^a (C)	Melt Ref ^a	Metals	Weight (kg)	
4	6.6	590	1395	933	1.49	Cu	5	Insulating brick
5	6.6	565	1403	966	1.46	Cu	5	Insulating brick
6	7.5	595	1386	955	1.45	Cu	5	Insulating brick
7 ^b	6.9	590	1403	947	1.44	U	10	Insulating brick
8a	6.9	610	1261	1010	1.25	Cu	5	Fume trap
8b	6.9	605	1401	1102	1.27	Cu	5	Fume trap
9	7.5	655	1386	1070	1.34	Cu	5	Fume trap with radiation shields 1 in. below crucible top.
10	7.5	675	1403	1105	1.36	Cu		Fume trap with radiation shields 1 in. below crucible top.
11a	7.5	675	1420	1060	1.44	U	10	Fume trap with radiation shields 1 in. below crucible top.
11b	7.5	665	1403	1038	1.35	U	10	Fume trap with radiation shields 1 in. below crucible top.
Na2	10.1	730	1370	1110	1.24	Na		Fume trap
Na3	6.9	646	1219	966	1.26	Na	0.04	Fume trap with radiation shields 1 in. below crucible top.
Na4	6.9	640	1219	955	1.27	Na	0.04	Fume trap with radiation shields 1 in. below crucible top.
Na5	6.9	660	1202	945	1.27	Na	0.04	Fume trap with radiation shields 1 in. below crucible top.
Na6	6.9	612	1200	943	1.28	Na	0.04	Fume trap with radiation shields 1 in. below crucible top.

^aReference thermocouple.

^bRebuilt furnace and reference thermocouple at end of this run.

FIGURE 47

CROSS-SECTIONAL VIEW OF INDUCTION MELT-REFINING CRUCIBLE

DIMENSIONS

- 1 AMERSIL TUBE -- $2\frac{3}{8}$ IN OD X $1\frac{3}{4}$ IN ID X $1\frac{7}{8}$ IN HIGH
- 2 GRAPHITE SUSCEPTOR -- $7\frac{1}{4}$ IN OD X $6\frac{1}{2}$ IN ID X $7\frac{1}{4}$ IN HIGH
- 3 MICRAMIC -- 1/4 IN THICK
- 4 ZIRCONIA BRICK -- 1/2 IN THICK
- 5 ZIRCONIA CRUCIBLE -- $6\frac{3}{8}$ IN OD X $5\frac{1}{8}$ IN ID X $1\frac{1}{8}$ IN HIGH
- 6 BORON NITRIDE -- $1\frac{1}{2}$ IN DIAMETER X $1\frac{1}{4}$ IN HIGH 1/8 IN DIAMETER HOLE 3/4 IN DEEP

within 1/2 inch of the top face. By insulating the thermocouple in this manner a reference temperature, which is lower than the melt temperature, can be obtained. This lower temperature allows the use of more stable thermocouple elements, i.e., chromel-alumel rather than platinum-rhodium or rhenium-molybdenum. An immersion (platinum-rhodium) thermocouple in the melt was used to calibrate the reference thermocouple unit.

The ratio of melt temperature to the reference temperature (boron nitride block) was determined in a series of runs for melt temperatures in the range 1200 to 1420 C and for different insulating top covers of the melt crucible. These runs are summarized in Table 48.

In Runs 4 to 7 the top of the crucible was insulated by a ceramic brick fitted in the top of the crucible. The ratio of the melt to the reference temperatures was 1.47 ± 0.02 . This variation of ± 0.02 would be equal to a variation of ± 20 C at a melt temperature of 1400 C.

The furnace was disassembled and examined at the end of Run 7. The Amersil tube had cracked, but not in a fashion that harmed the integrity of the furnace. The boron nitride reference thermocouple unit was found to be dimensionally and physically unchanged, although slightly discolored. The furnace was rebuilt and a new reference thermocouple unit installed.

Runs 8a, 8b and Na2 show the effect of greater heat loss resulting from the substitution of the fume trap for the insulating brick on the top of the furnace. The power requirements are higher and the melt/reference thermocouple ratio is lower. This indicates a higher heat loss. In Runs 9 to 11 and Na3 to Na6 this heat loss through the top of the furnace was reduced by the use of heat shields. When the heat shields were suspended one inch below the top of the crucible (Runs 9 to 11) the melt/reference thermocouple ratio was 1.35 ± 0.01 . When the shields were located one inch above the top of the crucible, the ratio decreased to 1.27 ± 0.01 . A decrease in this ratio is indicative of higher heat losses.

These experiments indicate that a reproducible reading can be obtained by use of this type of reference thermocouple unit for any given experimental setup. However, the reference thermocouple will have to be recalibrated for any change in the insulating characteristics of the system.

A preliminary experiment was performed to estimate the effect of fission product heating on charge temperature. The fission product heating was simulated by using resistance heaters placed in a mass of steel pins inside a crucible. The crucible was located in an enclosed furnace.

Sufficient steel pins, 2.5 kilograms, were used to equal the heat capacity of a 10-kilogram charge of uranium. The simulated fission product heat of 0.83 kw, furnished by the resistance heaters, was about one-half of that expected from 10 kilograms of two per cent burn-up fuel pins. The steady-state temperature for the center of the mass of pins was 650 C without the fume trap lip heater and 725 C with this heater on. Equilibrium was established in four and one-half hours without the lip heater.

It is planned to repeat this experiment using uranium pins and heat inputs up to 1.5 kw.

c. Fume Trap

(A. A. Chilenskas, M. A. Slawewski, T. F. Cannon)

The fume trap, as shown in Figure 54, ANL-5896, was used on all runs after number 7 (Table 48). The effect of heat shields suspended from the fume trap is indicated in section b above and in Table 48. The runs prefixed "Na" were runs made to determine the effect of a heated or unheated crucible lip on the fume trap operation. Previous work (ANL-5858, page 95) showed that better collection efficiencies were obtained from the fume trap when the lip was heated. Two runs (Na5 and Na6) were made to explore this premise further. In Run Na5 the lip was heated to 800 to 900 C and the 40-gram charge of sodium, placed in a massive steel container inside the zirconia crucible, was heated to 600 C. The bell jar and furnace was evacuated to less than one mm mercury. Over 90 weight per cent of the sodium was collected in the fume trap. In Run Na6 the procedure was repeated except that the lip was unheated. About one-third of the sodium was unaccounted for in the fume trap.

d. Material Testing

(L. F. Coleman and G. J. Bernstein)

The problems involved in operating commutator-type reversible electric motors in a dry argon atmosphere have not been satisfactorily solved. A number of manufacturer-recommended brush grades have been tested in two prototype motors without appreciable improvement. Both types have been sent out to have the commutators rhodium-plated in an effort to alleviate sparking.

A series of spark breakdown tests has been concluded. These tests determined the voltages necessary to initiate a spark between small rods in an argon atmosphere. The effects of radiation fields of one and 1000 roentgen/hour on the spark voltages were minor.

Samples of boron nitride, Rosite 3250, and Mycalex were irradiated in the Gamma-Irradiation Facility to a total dose of 10^9 roentgen with little effect on physical properties.

3. Laboratory and Service Building (P. Fineman)

Equipment bulletins and shop drawings for the laboratory and service building were checked and returned to various subcontractors and vendors of the Stewart Construction Company with our approval and/or comments.

A prototype fume hood for the evaporation of samples in the junior caves was constructed and is being tested. Its operation is based on parallel flow scrubbing of the fumes with water or basic solution.

The fabrication of the shielded sample-storage rack was completed. The rack is designed to be used in the sample-storage field and permits the storage of 29 sample holders (six samples per holder) and the selection of individual sample holders without removing the others.

The design of a shielded sample carrier for use with this storage rack was started. It will be a multi-purpose shield and will be used for transporting to the junior caves samples from the sample-storage field and the Fuel Cycle Facility.

One of the six cells in the junior caves is intended for temporary storage of samples. The bulk of the samples will be in metal containers about two inches in length by one inch in outside diameter. For temporary storage of these samples a steel unit, $16\frac{1}{2}$ inches wide by 40 inches long by 2 inches thick, was designed to hold 250 samples.

Liquid-Waste Treatment (P. Fineman)

The design of the primary equipment for the processing of the junior cave high-level activity, liquid-waste solutions is completed. These wastes will be adsorbed on vermiculite, stabilizing them sufficiently to permit their disposal in accordance with Idaho Operations Office requirements.

Items of equipment designed for the processing of these wastes include the following:

1. A 5-gallon capacity metering tank for liquid wastes.
2. A transfer shield for 30 and 55-gallon size drums, which is intended to be used for the intra-site transportation of stabilized high-level wastes to the National Reactor Test Station burial site. Accessory equipment for the remote removal and handling of drums from the shield has also been designed.

VI. ANALYTICAL RESEARCH AND SERVICES

Coprecipitation of plutonium fluoride with lanthanum fluoride has been demonstrated to be a satisfactory method for separating "fissium" constituents from plutonium prior to its spectrophotometric determination as the nitrate.

Three indirect chemical methods for the determination of 100-microgram quantities of plutonium show promise. Reductions of plutonium (VI) with uranium (IV), iodide, and iron (II) will be followed by polarographic or spectrophotometric assays of the reaction products.

The selective solution of minor alloying constituents from bismuth alloys by leaching amalgams with hydrochloric-hydrofluoric acid mixtures has been extended to use with cerium, magnesium, zirconium, and niobium alloys.

In the development and modification of instruments for use in the EBR-II analytical cave facility, spectrophotometer modifications have been made; ultrasonic cleaning of contaminated cave equipment has been demonstrated, and a remote pipetter has been developed and tested. Additional methods have been selected, tested, and written up for use in the EBR-II analytical facility.

The thermal neutron capture cross section of cesium-137 is being determined by irradiating cesium-137 targets and counting the cesium-138 in the presence of the target material. The determination of fission product cesium-137 is commonly used as a measure of the number of fissions which have occurred in reactor fuels. This cross section will indicate whether a significant amount of the cesium-137 is consumed in the reactor. The present work indicates that the neutron capture cross section of cesium-137 is low enough so that no effect on cesium-137 content will be observed in the burn-up determinations.

A. Analytical Service and Development (R. P. Larsen)

1. Plutonium Analyses

a. Spectrophotometric Determination of Plutonium as the Nitrate Complex (C. A. Seils and R. M. Clarke)

A method for the determination of plutonium in plutonium "fissium" alloys was reported in ANL-5820, page 142. The plutonium was separated from the uranium and fission elements by a hydrochloric acid - TBP solvent extraction procedure and determined spectrophotometrically

as the nitrate. The difficulties of carrying out extraction separations within the confines of a glove box prompted a search for a more convenient method of separation.

The coprecipitation of 2 to 10 milligrams of plutonium (III) fluoride with lanthanum fluoride had previously been demonstrated to be quantitative but unsuitable for use in redox titrations because uranium was partially carried. Since an equal molar ratio of uranium to plutonium can be tolerated in the spectrophotometric nitrate method, consideration was given to the use of the lanthanum fluoride precipitation as a substitute for the TBP extraction. On dissolving the precipitated standards in aluminum nitrate-nitric acid the absorbance measurements were consistently 56 per cent lower than the values obtained with direct standards. Probably the absorbance of $\text{PuF}(\text{NO}_3)_3$ was being measured rather than $\text{Pu}(\text{NO}_3)_4$. The use of zirconyl nitrate instead of aluminum nitrate overcame this difficulty. An early study of the fluoride complexes of plutonium by Kroner reported by Seaborg and Katz³⁰ had noted the effect of zirconium on plutonium fluoride complexes. The absorbance measurements on zirconyl nitrate-nitric acid dissolutions of precipitated standards were the same as those obtained on direct standards; the separation from the fission elements and uranium in "fissium" was quite satisfactory.

b. The Chemical Determination of Submilligram Amounts of Plutonium

Because of changes in isotopic composition, the radiochemical determination of plutonium in plutonium-bearing reactor fuels can only be made by combining the information obtained in three separate determinations: plutonium alpha, alpha pulse, and mass spectrometric analyses. The preparation of the mass spectrometric samples is particularly arduous, requiring a high beta-gamma decontamination and meticulous care to prevent cross contamination. Since a sensitive method of chemical analysis would obviate the need for three separate determinations, work has been initiated to meet this need. Three indirect methods have been studied briefly; each shows promise. They are summarized below.

Indirect Polarographic Methods
(A. M. Wilson,* R. J. Meyer)

This method is based on the oxidation of plutonium to the hexavalent state with perchloric acid, the reduction of plutonium (VI) to plutonium (III) with a uranium (IV) fluoride solution, and the polarographic determination of the oxidation product uranium (VI). Preliminary results obtained for pure plutonium are given in Table 49.

³⁰ Seaborg, G. T. and Katz, J. J., "The Actinide Elements," McGraw-Hill, New York (1954).

*Summer employee from Northwestern University.

Table 49

THE INDIRECT POLAROGRAPHIC DETERMINATION
OF PLUTONIUM

<u>Determinations</u>	<u>Final Volume</u>	<u>Plutonium (μg)</u>		<u>Std Dev (%)</u>
		<u>Taken</u>	<u>Found</u>	
6	1	10.0	10.4	± 10
5	5	200	199	± 2.5
3	5	496	510	± 1.7

Experience with the polarographic determination of uranium (VI) prompted the use of uranium (IV) as the reductant. Consideration of other reductants, particularly ferrous, will also be made since it is appreciated that the use of uranium (IV) necessitates the complete removal of both uranium and iron from the plutonium prior to the perchloric acid oxidation.

Indirect Spectrophotometric Methods
(J. J. McCown and A. M. Wilson)

The reduction of plutonium (VI) with excess standard ferrous sulfate and the determination of the unoxidized ferrous with 1-10-orthophenanthroline will also provide a plutonium assay. Prior knowledge of the approximate plutonium concentration is necessary, but a quick alpha assay can provide this information. No interference from iron, a common and difficult to separate contaminant, would be encountered. Preliminary testing of the method is summarized in Table 50.

Table 50

THE SPECTROPHOTOMETRIC DETERMINATION
OF PLUTONIUM (VI) WITH FERROUS
ORTHOPHENANTHROLINE

<u>Plutonium (μg)</u>		<u>% Error</u>
<u>Taken</u>	<u>Found</u>	
110	114	+ 4
110	112	+ 2
110	103	- 7
25	24	- 4
25	25	0
25	28	+10

Kraus and Moore³¹ have reported that plutonium (VI) is rapidly reduced by iodide to plutonium (V) at a pH of 3.5 and that further reduction is very slow. By extracting the iodine with carbon tetrachloride a direct determination of the iodine equivalent of plutonium can be made spectrophotometrically. Preliminary results are shown in Table 51.

Table 51

THE SPECTROPHOTOMETRIC DETERMINATION
OF PLUTONIUM (VI) WITH IODIDE

<u>Plutonium (μg)</u>		
<u>Taken</u>	<u>Found</u>	<u>% Error</u>
250	230	-9
250	244	-4
250	249	-0.5

Strong oxidants formed during the perchloric acid fuming will interfere in each of these methods, but it is expected that these ions will be separable by the established precipitation, solvent extraction, or ion exchange methods.

2. The Selective Solution of Cerium, Magnesium, Zirconium, and Niobium from Bismuth Alloys
(R. J. Meyer)

The amalgam-leach separation used to dissolve uranium selectively from bismuth alloys (ANL-5858, page 127) has been extended to cerium, magnesium, zirconium, and niobium. The magnesium and zirconium will be added to the LMFR fuel, while the cerium and niobium will be there as fission products.

Active zirconium, niobium, and cerium were used to check the leaching of these constituents; magnesium was checked with an EDTA titration.

Before leaching, each bismuth alloy was homogenized by grinding and a portion was dissolved in nitric acid as a control. A small amount of hydrofluoric acid was also added in the case of the zirconium alloy. Another portion of each alloy was treated by amalgamating the bismuth and leaching it with a 4 M hydrochloric acid - 0.5 M hydrochloric acid solution. For the cerium alloy the fluoride was omitted. A comparison of the nitric acid and amalgam-leach dissolution is shown in Table 52. The active samples were gamma counted in a well-type scintillation counter.

³¹Kraus, K. A. and Moore, G. E., "The Transuranium Elements," National Nuclear Energy Series Paper 4.19, McGraw-Hill, New York, 1949.

Table 52

A COMPARISON OF THE NITRIC ACID AND AMALGAM-LEACH
DISSOLUTIONS OF BISMUTH ALLOYS

<u>Constituent Leached</u>	<u>Nitric Acid Diss (cpm/g)</u>	<u>Amalgam-Leach Diss (cpm/g)</u>
Cesium-144	5.25×10^4	5.42×10^4
Zirconium-95 - Niobium-95	1.35×10^4	1.44×10^4

To check the recovery of magnesium by the amalgam-leach method an amalgam of magnesium was prepared from ribbon and then leached with 4 M hydrochloric acid. Aliquots of the leach solution were titrated with standard EDTA using Eriochrome Black T as indicator. Four titrations gave an average value of 4.31 ± 0.05 mg of magnesium as compared to the known value of 4.26 mg of magnesium.

These results show that cerium, magnesium, zirconium, and niobium are quantitatively leached from a bismuth amalgam. Using this procedure it has been possible to determine magnesium and fission product zirconium by conventional means.

3. EBR-II Analytical Facility
(J. J. McCown and W. R. Sovereign)

a. Instrumentation

The program for developing instruments and apparatus for use in the junior caves, as reported in ANL-5789, page 135, is being continued. Recent developments include the use of a Beckman C colorimeter in place of the Beckman B spectrophotometer for colorimetric determinations; the use of an ultrasonic cleaner inside the caves for decontaminating manipulator tongs and special glassware; and the design and construction of a motor-driven, remotely operated micropipetter.

Although the Beckman C colorimeter is less accurate than the Model B spectrophotometer, it has the following advantages for use in remote work:

1. The optical block is removable and can be placed inside a cave, while the amplifier and galvanometer components remain outside.
2. The over-all cost is approximately one-fifth that of the Model B, so that in case of gross contamination of the instrument it can be discarded.

3. The space required in the cave for using the Model C is approximately one-tenth that required for the Model B.

"On the spot" decontamination of small cave accessories and chemical equipment with an ultrasonic cleaner has been found to be very satisfactory. A Sonogen Model AP10B ultrasonic cleaner with a one-half-gallon capacity tank and transducer unit was installed in the junior cave and connected through the caves operating face to the generating unit located inside. In Table 53 "before" and "after" activity levels are given for a number of items which were decontaminated with this equipment.

Table 53

ULTRASONIC DECONTAMINATION OF CAVE EQUIPMENT

<u>Type of Equipment</u>	<u>Type of Activity</u>	<u>Radiation Level</u>		<u>Time Required (min)</u>
		<u>Before</u>	<u>After</u>	
Diagonal cutters	(β , γ)	200 mr	~5 mr	5
10-in. Forceps	(β , γ)	250 mr	~5 mr	5
Platinum Cathode	(β , γ)	750 mr	20 mr	5
Glass Filter Chimney	(β , γ)	200 mr	0	2
Stirring Rod	(α)	>40 M	0	2
Separatory Funnel Clamp	(α)	20 M	0	2
Model of Manipulator Jaws	(β , γ)	1.5 R	15 mr	3
Model of Manipulator Jaws	(α)	>40 M	<2 M	3

The remote micropipetter is illustrated in Figure 48. A six-position rheostat controls the speed of the dc motor, thus making it possible to vary the fill rate. On position 2 the volume displacement is 10 λ per minute; on position 6, 1000 λ per minute. Using this unit it is possible to pipet from 10 to 1000 λ as accurately as can be done by hand.

b. Analytical Methods Development

The analytical methods that will be used for EBR-II processing control were summarized in ANL-5789, page 136, Table 36. Methods developed in the Analytical Service Laboratory and methods reported in the literature since that time have resulted in additions to the proposed methods for EBR-II. These are listed in Table 54.

In addition to the processing control samples a considerable number of analyses will be required on water samples from the EBR-II steam system. The analytical methods which will be used for water analysis are listed in Table 55.

FIGURE 48 MICRO PIPETTER

Table 54

ADDITIONAL ANALYTICAL METHODS^a FOR
EBR-II PROCESSING CONTROL

Element	Method	Separation
Uranium	Polarographic	Mercury cathode electrolysis
Palladium	Polarographic	Cation exchange
Palladium	Colorimetric - 2 nitroso - 1 naphthol	Toluene extraction
Molybdenum	Polarographic	None
Rhodium	Colorimetric - stannous bromide	Anion exchange
Magnesium	Micro volumetric - EDTA	Diethyldithiocarbamate extraction
Zinc	Volumetric - EDTA	None

^aSee ANL-5789, page 136, for description of analytical methods.

Table 55

ANALYTICAL METHODS FOR EBR-II STEAM
SYSTEM WATER ANALYSIS

<u>Element</u>	<u>Method</u>	<u>Separation</u>
Dissolved oxygen	Colorimetric - indigo carmine	None
Chloride	Colorimetric - diphenyl carbazone	None
Iron	Polarographic	None
	Colorimetric - bathophenanthroline	None
Copper	Polarographic	None
	Colorimetric - bathocuproine	None
Calcium	Volumetric - EDTA	None
Hydrazine	Colorimetric - p-dimethylamino-benzaldehyde	None

A manual of EBR-II Analytical Methods has been prepared. It now contains 22 methods, both radiochemical and wet chemical. Additional methods are currently being prepared in manual form.

B. Analytical Research
(C. E. Crouthamel)

1. Thermal Neutron Capture Cross Section of Cesium-137
(D. C. Stupegia)

Targets containing about 10^8 dps of cesium-137 were irradiated in CP-5, at a thermal flux of about 10^{13} n/(sq cm)(sec), for around 15 minutes. The resulting 32-minute cesium-138 was counted on the 256-channel gamma spectrometer with its 4 in. x 4 in. cylindrical sodium iodide crystal detector. Only the highest energy gammas of cesium-138, namely, the 2.21 and 2.62 Mev gammas, can be seen in the presence of the effects caused by the much more intense 0.661-Mev gamma of cesium-137.

Experimental Details: The cesium-137 targets were prepared from the material, an acid solution of cesium chloride, supplied by the ORNL Radioisotopes Division. Isotopically, the cesium was 44 per cent cesium-133, 20 per cent cesium-135, and 36 per cent cesium-137. Impurities, mainly iron, rubidium, and sodium, were present. Chlorine was removed by evaporation with nitric acid, since chlorine-38 would interfere with cesium-138, both in gamma energies and half-life. The target was made by evaporating the cesium nitrate onto 0.001-in. mylar and covering with another mylar foil. The targets were counted by means of a single-channel gamma analyzer with a 4-in. diameter and 3-in. height sodium

iodide crystal. Since the disintegration rate was so high, the source to crystal distance had to be about 21 feet. The count was an integrated count upwards from just below the 0.661-Mev gamma peak. The crystal was calibrated by cesium-137 samples of known activity, these having been determined ultimately by 4π - β counting. In the irradiations, gold wire was used as a flux monitor, the gold-198 activity being determined by 4π - β counting and by absolute gamma counting.

Of the many gammas in the decay of cesium-138, only the 2.21 and 2.62-Mev gammas can be seen in the background hash produced by the secondary effects of betas and gammas of cesium-137. The fraction of decays giving these gammas is known: 18 per cent give the 2.21 Mev and 9 per cent give the 2.62 Mev. Counting efficiencies for these gammas have been found. Counting was done through thick lead absorbers (2 in. or 2.5 in.), each centimeter of which attenuates the cesium-137 gamma to 32 per cent and the cesium-138 gamma to about 60 per cent of the initial values. Further, the analyzer was set up to discriminate electronically against analyzing energies below about 1.8 Mev. Still, it is difficult to extract the data in the presence of the cesium-137.

Results: Six irradiations were carried out and most of the data analyzed. In the first two runs the cross section was about 0.26×10^{-24} sq cm, on the basis of the 2.62-Mev gamma. In runs 3, 4, and 6, on the basis of the 2.21-Mev gamma, the values averaged to $0.10 \pm 0.01 \times 10^{-24}$ sq cm. The data are summarized in Table 56. The 2.62-Mev gamma results appear to be in error, since the determinations at 2.21-Mev gamma appear to be more reliable.

Table 56

THERMAL NEUTRON CAPTURE CROSS SECTION OF CESIUM-137

Irradiations in CP-5 at Thermal Flux $\sim 10^{13}$ n/(sq cm)(sec)
 Targets contain $\sim 10^8$ dps of Cs-137
 Irradiation times ~ 15 min

Irradiation	Thermal Neutron Capture Cross Section (10^{-24} sq cm)	
	From 2.21-Mev gamma	From 2.62-Mev gamma
1	-a	0.27 ± 0.02
2	-a	0.26 ± 0.02
3	0.0923 ± 0.003	() ^a
4	0.0938 ± 0.003	() ^a
5	-a	-a
6	0.13 ± 0.006	() ^a

^aParenthesis indicate data still to be analyzed, and blanks indicate failure to resolve the gamma peak from background.

VII. ROUTINE OPERATIONS (H. G. Swope)

A. Waste Processing

1. Operations

(J. Harast, K. Bremer and F. Testa)

The total amount of radioactive liquid wastes processed from July through September, 1958, was 43,000 gallons. The volumes processed by evaporation were 22,700 gallons; by filtration 8,000; by cation exchange 8,000; by flocculation 900; by absorption into vermiculite 900; and 2,500 gallons were allowed to decay.

Of the 8,000 gallons processed by filtration followed by cation exchange, 6,800 gallons were from the EBWR.

2. Laboratory

(H. G. Swope, C. Ryberg, C. Wade and B. Tamulionis)

Several special problems were investigated. One was to develop an alternative procedure for handling plutonium and "hot" wastes which heretofore had been made into concrete in a remote-control cave in D205. This cave has been dismantled to make room for other work. The Waste Processing Committee decided that wastes of this sort, insofar as possible, should be adsorbed into vermiculite and disposed of as solid active wastes. Since a variety of solvents and chemicals may be found in the wastes, experiments were made at room temperature to determine the amount of liquid which could be absorbed, as well as the effect of various reagents on the vermiculite. The results indicate that of the concentrated acids, only sulfuric or phosphoric acids can be adsorbed without dilution and/or neutralization. When 6 N acids were used, only hydrochloric acid and nitric acid could be used without dilution and/or neutralization. All of the alkalies tested were satisfactory, i.e., five and 50 per cent sodium hydroxide and concentrated ammonium hydroxide. All of the organics tested (acetone, ethyl and methyl alcohols, carbon tetrachloride and kerosene) appear satisfactory, even after standing at room temperature for two months. Tests will be made to see if heat or cold have any effect on these reagents in vermiculite when allowed to stand for long periods.

The other special problem has been the processing of EBWR reactor wastes. It has been necessary to process 6,800 gallons of wastes from EBWR, which after initial decay still had 2.6×10^3 cpm/ml beta-gamma activity and 1.4 cpm/ml alpha activity. Total solids were 82 ppm, pH 6.8. This waste presumably contained mostly cobalt-58.

It was determined in one-half-inch laboratory columns that at the as-received pH (6.8) decontamination factors of 10 were obtained using a cation resin (HCR-H⁺) and only 18 for a mixed bed (1 part HCR-H⁺; 2 parts SAR-OH) and the capacity of the latter was only 125 gal/cu ft. When the pH was lowered to 2.5, no improvement was found on the cation column, but the mixed bed gave a decontamination factor of $>10^3$ up to a capacity of 600 gal/cu ft.

B. Gamma-Irradiation Facility

(H. G. Swope, J. Harast, R. Juvinall, T. Emmering, J. Gates, N. Ondracek and B. Kullen)

The numbers of samples irradiated in Rack M-1 during July, August and September are shown in Table 57. The large circular rack, M-2, was used only once during this period.

Table 57

SUMMARY OF NUMBER OF SAMPLES AND UNITS FOR JULY, AUGUST AND SEPTEMBER IN HIGH-LEVEL GAMMA-IRRADIATION FACILITY

	<u>Rack M-1</u>											
	<u>No. of Samples^a</u>			<u>Total Urn Units Based on Rads^b</u>								
				<u>Day</u>			<u>Night</u>			<u>Special Dosimetry</u>		
	<u>July</u>	<u>Aug</u>	<u>Sept</u>	<u>July</u>	<u>Aug</u>	<u>Sept</u>	<u>July</u>	<u>Aug</u>	<u>Sept</u>	<u>July</u>	<u>Aug</u>	<u>Sept</u>
QMF and CI	581	397	747	712	545	1111	4	7	7	140	42	128
Industry	35	15	22	47	53	90	307	328	1600	18	0	0
Educ Inst	17	4	2	50	45	18	356	457	74	0	0	0
ANL	57	19	16	213	165	155	897	843	395	175	23	114
Totals	<u>690</u>	<u>435</u>	<u>787</u>	<u>1022</u>	<u>808</u>	<u>1374</u>	<u>1564</u>	<u>1635</u>	<u>2076</u>	<u>333</u>	<u>65</u>	<u>242</u>

^aEquivalent to a No. 2 sized can.

^bOne urn unit in Rack M-1 = 2×10^6 r.